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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
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PART I.

Organic Chemistry.

**Bromination with Aluminium Bromide in the Aliphatic
Series.** By A. Mouneyrat (*Compt. rend.*, 1898, 127, 109—111.
Compare Abstr., 1898, i, 613).—Aluminium bromide behaves as a
powerful brominating agent, because, like aluminium chloride, it has
the property of producing double linkings in alkylic haloids. When
it is heated with dry ethylenic dibromide, hydrogen bromide and
acetylene are obtained, and if bromine is also present, this combines
additively with the unsaturated compound thus produced. The author
shows that, by means of aluminium bromide, ethylic bromide can be
successively converted into ethylenic dibromide, acetylene tetra-
bromide, and hexabromethane. By this method, hexabromethane is
most readily prepared from acetylene tetrabromide, the yield obtained
being 65—70 per cent.   G. T. M.

Action of Chloroform on Aqueous Alkali. By Johannes
Thiele and Frankland Dent (*Annalen*, 1898, 302, 273—274 Com-
pare Desgrez, Abstr., 1898, i, 166).—Geuther has observed that
chloroform yields carbonic oxide with aqueous and alcoholic alkalis
(*Annalen*, 1862, 123, 121); under conditions described by the
authors, it is found that quantities of chloroform varying between
21 per cent. and 66 per cent. are convertible into formic acid through
the action of caustic soda.   M. O. F.

Decomposition of Iodoform Solutions. By J. Bougault
(*J. Pharm.*, 1898, [vi], 8, 213—214).—On exposing a sealed glass
vessel containing a solution of iodoform in ether together with
mercury or centinormal aqueous sodium thiosulphate to bright sun-
light, iodine is initially liberated in the ethereal layer ; on shaking,

however, the iodine is removed, but on further exposure more sodium is set free, which can be removed as before. Ultimately, however, no more iodine is liberated, even on long exposure to light; from this it is concluded that light alone does not affect iodoform, but that its decomposition is due to oxidation. This view is confirmed by the presence of a considerable quantity of formic acid in an ethereal solution of iodoform from which iodine has separated.   W. A. D.
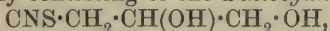
Composition and Solubility of Sodium Ferrocyanide. By JAMES T. CONROY (*J. Soc. Chem. Ind.*, 1898, **17**, 103—106).—Analyses of several specimens of pure sodium ferrocyanide show that it contains $10H_2O$. Its solubility at various temperatures was determined by means of a special form of apparatus; an excess of the salt was agitated by means of a current of air with water contained in a large test-tube surrounded by water at a known temperature. The test-tube was connected by a glass-tube with a weighing bottle completely immersed in the water of the heating bath, so that by suction at a second tube with which the weighing bottle was provided, the saturated solution of the salt could be transferred to the latter; by determining the weight of the solution thus transferred, and the quantity of salt it left on evaporation, the solubility was ascertained. The tube connecting the dissolving tube with the weighing bottle was provided with a filtering plug by which the liquid transferred could be freed from undissolved material. Curves are given which show the solubility in water of sodium and potassium ferrocyanides at temperatures between 15° and 100°; it appears that, whereas the solubility of anhydrous potassium ferrocyanide is always greater than that of the anhydrous sodium salt, hydrated potassium ferrocyanide, $K_4FeC_6N_6 + 3H_2O$, is more soluble than the sodium salt, $Na_4FeC_6N_6 + 10H_2O$, only at temperatures below 54°.

On adding 50 grams of crystalline sodium ferrocyanide dissolved in water (50 c.c.) to a solution of 60 grams of potassium carbonate in 60 c.c. of water, 93 per cent. of the potassium ferrocyanide theoretically possible separates on standing. When a solution of 50 grams of sodium carbonate in 150 c.c. of water is added to 50 grams of potassium ferrocyanide dissolved in 100 c.c. of water, no crystals separate on standing, but on evaporating the liquid to one-half its volume, sodium and potassium ferrocyanide crystallise together. When, however, an aqueous solution of 60 grams of sodium chloride and 50 grams of potassium ferrocyanide is allowed to crystallise, 91 per cent. of the sodium ferrocyanide theoretically possible is obtained; on the other hand, a solution of 60 grams of potassium chloride and 50 grams of sodium ferrocyanide deposits 60 per cent. of the theoretical quantity of potassium ferrocyanide. These phenomena are elucidated by the values given of the solubility of potassium and sodium ferrocyanide in solutions of the alkali chlorides and carbonates; at ordinary temperatures, potassium ferrocyanide is very slightly soluble in saturated aqueous potassium chloride, and sodium ferrocyanide in sodium chloride solution. Similarly, each ferrocyanide is very sparingly soluble in a solution of the carbonate of its own metal.
          W. A. D.

Action of Metallic Thiocyanates on Aliphatic Chlorhydrins.
By Wilber D. Engle (*J. Amer. Chem. Soc.*, 1898, **20**, 668—678).—
On heating α-chloropropylenic glycol, $CH_2Cl \cdot CH(OH) \cdot CH_2 \cdot OH$ (14
grams), dissolved in 95 per cent. alcohol, with potassium thiocyanate
(13 grams) during 4 days on the water-bath, potassium chloride
gradually separates; on removing the latter, and again heating, a
white, resinous *substance* separates, which is insoluble in all organic
solvents, and gives none of the reactions of organic thiocyanates. It
contains $C = 40 \cdot 145$; $H = 5 \cdot 168$; $N = 7 \cdot 560$; $S = 27 \cdot 281$, and $O = 19 \cdot 846$
per cent.; it is not affected by hydrochloric or sulphuric acid, and by
aqueous ammonia or potash, but is decomposed by bromine, giving a
tarry product, and is oxidised by concentrated nitric acid to sulphuric
and oxalic acids. A small amount of an oil having a garlic-like
odour, and apparently consisting of the α-*thiocyanhydrin*,
$$CNS \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH,$$
is formed along with the white substance above described, but on
attempting to purify it, it is immediately converted into the latter.
The same products are obtained, in similar proportion, by heating
α-chloropropylenic glycol with potassium thiocyanate in sealed tubes
at 110—115°; at 120°, however, there is a considerable amount of
decomposition.

When an alcoholic solution of αβ-dibromopropylic alcohol (40
grams) is heated with potassium thiocyanate (37 grams) during 6
days, potassium bromide separates, and on removing the alcohol by
evaporation, washing with water, and extracting with ether, 10 c.c. of
a dark coloured oil is obtained, which appears to consist principally
of the *dithiocyanhydrin*, $CNS \cdot CH_2 \cdot CH(CNS) \cdot CH_2 \cdot OH$; it cannot be
purified by distillation as it immediately resinifies, but its identity is
established by its yielding *imidomethanepropylic alcohol bisulphide
hydrochloride*, $OH \cdot CH_2 \cdot \underset{CH_2 \cdot S}{\overset{CH--S}{\underset{|}{C}}} {>} C \vdots NH, HCl$, when reduced by means
of tin and hydrochloric acid; this separates from alcohol in
transparent, colourless, tetragonal crystals, whilst its *tin* double salt
forms large octahedra. The dithiocyanhydrin described can be more
rapidly prepared by heating the mixture mentioned above for 8 hours
at 110—115°; at higher temperatures, decomposition occurs, and in
all cases a considerable amount of a resinous *substance*, similar to that
obtained from α-chloropropylenic glycol, is formed. The α-*acetyldithio-
cyanhydrin*, obtained by heating αβ-dibromopropylic acetate (17 grams)
with potassium thiocyanate (13 grams) and alcohol (10 c.c.) for
4 hours at 120°, is a red oil which cannot be distilled.
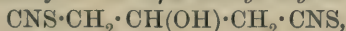
Only a small quantity of the αγ-*dithiocyanhydrin*,
$$CNS \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot CNS,$$
is formed when αγ-dichlorisopropylic alcohol is heated with alcoholic
potassium thiocyanate, either on the water bath during 4 days, or in
a sealed tube for 2 hours at 175°; the principal product in each
case is a yellow, sponge-like *resin*. A similar *substance* is obtained
from αγ-dichlorisopropylic acetate under the same conditions.

Potassium thiocyanate readily interacts with epichlorhydrin and

epibromhydrin at 40—50°, a good yield of the corresponding *epithio-cyanhydrin*, $\text{CNS·CH}_2\text{·CH}\underset{\displaystyle \text{CH}_2}{\big|}\!\!>\!\!O$, being obtained; when freed from

potassium thiocyanate by washing with water, and from condensation products by dissolving in ether, the cyanhydrin is obtained as a transparent, dark red liquid with an odour of garlic. It cannot be distilled, and closely resembles the cyanhydrins already described; when treated with hydrogen sulphide under a pressure of 960 mm., it does not yield a derivative of carbamic acid, but a thick, syrupy liquid, probably a sulphide. On heating epithiocyanhydrin with an excess of methylic iodide at 100° for 6 hours, *epihydrindimethylsulphine iodide*,

$$O\!\!<\!\!\underset{\displaystyle \text{CH·CH}_2\text{·SMe}_2\text{I},}{\overset{\displaystyle \text{CH}_2}{|}}$$
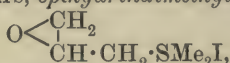
is formed; it crystallises from water in monosymmetric plates, and decomposes at 195—200° without melting.   W. A. D.

Betaine contained in the Root of Althæa Officinalis. By N. A. ORLOFF (*Chem. Centr.*, 1898, i, 37; from *Pharm. Zeit. Russ.*, **36**, 631—632).—Betaine can be obtained from the aqueous extract of the root of *Althæa officinalis* after removing the asparagine by precipitating it with nitric acid and sodium phosphomolybdate; the free base obtained by treating the precipitate with barium hydroxide forms colourless crystals, is soluble in water and alcohol, and insoluble in ether. The hydrochloride is easily crystallised, and does not change on exposure to the air. With potassium dichromate solution and hydrochloric acid, betaine does not exhibit any colour reaction. It is precipitated by picric acid, zinc chloride, and auric chloride, but not by tannin; the aurochloride, $C_5H_{11}NO_2,HAuCl_4$, crystallises in microscopic plates, or in short crystals arranged in the form of a cross.
E. W. W.

Ketonic Bases. By ERNST SCHMIDT (*Arch. Pharm.*, 1898, **236**, 334—343. Compare following abstract).—The following compounds containing ketonic groups, which have been prepared by the action of trimethylamine or pyridine on monochloracetone and bromacetophenone, namely, *trimethylacetonylammonium chloride, pyridylacetonyl chloride, trimethylacetophenylammonium bromide,* and *pyridylacetophenyl bromide*, readily yield oximes on treatment with hydroxylamine. The reagents usually employed for producing the Beckmann rearrangement do not act on these oximes in the usual manner; phosphorus pentachloride alone appears to produce the rearrangement, but owing to the instability of the bases formed, it could not be definitely decided whether this is the case or not. The oximes of trimethylacetophenylammonium bromide and pyridylacetophenyl bromide are converted by boiling with acetic chloride into monacetyl derivatives, whereas in closed vessels this reagent has no action on them.

A detailed account of the physiological action of these ketonic bases and their oximes is given.

The action of primary, secondary, and other tertiary bases on monochloracetone and bromacetophenone has been studied, and the following

additive products prepared. *Quinolyl-* and *isoquinolyl-acetonyl chloride* compounds from quinoline, strychnine, and hydrastine with brom-acetophenone; *acetonylpiperidine hydrochloride; acetonylmethylpyridine chloride; acetophenylpiperidine hydrobromide; diacetophenylpiperidine bromide; dimethylacetophenylammonium bromide; dimethyldiacetophenyl-ammonium bromide; methylacetophenylammonium bromide; methyldi-acetophenylammonium bromide,* and possibly *methyltriacetophenylammo-nium bromide.*   A. W. C.

Trimethylacetonylammonium Chloride. By A. L. C. Furnée (*Arch. Pharm.,* 1898, **236,** 343—353. Compare preceding abstract). —Trimethylacetonylammonium chloride (coprine chloride),

$$CH_2Ac \cdot NMe_3Cl,$$
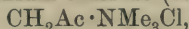
first prepared by Niemilowicz (*Monatsh.,* 1886, **7,** 242) by the interaction of monochloracetone and trimethylamine, is a crystalline substance. The *platinochloride* forms yellowish-red needles melting at 238—240°; the *aurochloride* crystallises in beautiful, yellow needles melting at 139·5°. The *oxime* separates from a mixture of alcohol and ethylic acetate in colourless plates melting at 212°, and is readily soluble in water and alcohol, but almost insoluble in cold ether and ethylic acetate; it yields an *aurochloride* crystallising in fine yellow needles melting at 170—171°, and a *platinochloride* in yellowish-red crystals melting at 206°.

When reduced with sodium amalgam, the oxime is reconverted into trimethylacetonylammonium chloride; only on one occasion was a substance obtained which, from analysis of its *aurochloride,* melting at 156°, and its *platinochloride,* melting at 210°, appeared to be the desired amine.

Attempts to bring about the Beckmann rearrangement led to the following results. The oxime is not altered by heating with 25 per cent. hydrochloric acid; or by concentrated sulphuric acid or acetic chloride at 100° in sealed tubes. Trimethylacetonylammonium chloride is re-formed when the oxime is treated with concentrated hydrochloric acid either at 0° or when heated with it in sealed tubes at 150°; and on heating with concentrated sulphuric acid at 100° for 10 minutes.

When boiled with acetic chloride or acetic anhydride, an *acetyl* derivative is obtained as a radiating, crystalline mass, giving a beautiful, yellow crystalline *aurochloride* melting at 120°. On boiling with benzoic chloride, a *benzoyl* derivative is obtained; its *aurochloride* forms yellow crystals melting at 165°, whilst the *platinochloride* melts at 212°.

When the oxime is dissolved in phosphorus oxychloride and phos-phorus pentachloride slowly added, rearrangement takes place, a reaction which is being further studied. The product gives an *aurochloride* crystallising from water in star-shaped groups of needles melting at 128°, and a *platinochloride* separating in needles and melt-ing at 227°.   A. W. C.

Free Chitosamine. By Cornelis A. Lobry de Bruyn (*Ber.,* 1898, **31,** 2476—2477).—In connection with Breuer's recent note on free chitosamine (Abstr., 1898, i, 620), the author draws attention to

the fact that the base had already been isolated (L. de Bruyn and Alberda van Ekenstein, *Kong. Akad. Wiss. Amsterdam*, January 2, 1897), and gives an extract from the published note.

The base was isolated by acting on the powdered hydrochloride with sodium methoxide dissolved in methylic alcohol, and was obtained in the form of needles by precipitation with dry ether. It is very hygroscopic, and dissolves readily in water. When its solution in methylic alcohol is kept, it furnishes a crystalline substance which is identical with that obtained by acting with ammonia on a solution of fructose in methylic alcohol. It follows that the sugar from which chitosamine is derived is related to fructose.

Chitosamine hydrochloride, when treated with silver carbonate, yields a substance which gives glucosazone with phenylhydrazine, and a well-crystallised polyacetate on treatment with acetic chloride.

A. L.

Compounds of Hexamethylenetetramine (Urotropine). By BRUNO GRÜTZNER (*Arch. Pharm.*, 1898, **236**, 370—381).—Hexamethylenetetramine has been obtained by Butlerow by passing ammonia over methylene oxide, and is now used as a medicine under the name of urotropine. The author prepared the substance according to Hofmann's directions, by evaporating a solution of formaldehyde with excess of ammonia; during the process, it was observed that, on warming a cold saturated aqueous solution of the base, a precipitate is formed, which disappears again on cooling; this is possibly due to the formation of a compound with water.

The following compounds of hexamethylenetetramine have been prepared. The *hydrobromide*, slender white needles, very soluble in water; the *hydriodide*, which is decomposed by water, with separation of iodine; the *arsenate*, $C_6H_{12}N_4,H_3AsO_4 + \frac{1}{2}H_2O$, glistening, silken crystals; *hexamethyleneamine silver nitrate*, $C_6H_{12}N_4,AgNO_3$, microscopic, rhombic plates, soluble in water with a neutral reaction; by the action of silver nitrate on hexamethyleneamine in molecular proportion in presence of nitric acid, a mixture of the compound, $C_6H_{12}N_4,AgNO_3,HNO_3$, and the above substance is obtained as a microcrystalline precipitate; *hexamethyleneamine mercuric chloride*, $C_6H_{12}N_4(HgCl_2)_2$, white needles, which, when powdered, are strongly electric; the *compound* $C_6H_{12}N_4,HgCl_2$, obtained as a crystalline precipitate, by adding mercuric chloride (1 mol.) to an alcoholic solution of the base (1 mol.); *hexamethyleneamine hydrochloride mercuric chloride*, $(C_6H_{12}N_4,HCl)_2(HgCl_2)_3$, a voluminous precipitate of microscopic, flat, monoclinic plates; *hexamethyleneamine mercuric iodide*, $C_6H_{12}N_4,HgI_2$, white, glistening needles; *hexamethyleneamine mercuric cyanide*, crystalline precipitate of hexagonal pyramids, readily soluble in water and alcohol; *hexamethyleneamine magnesium chloride*, $(C_6H_{12}N_4)_2,MgCl_2 + 9H_2O$, triclinic prisms soluble in water with a faintly alkaline reaction; *hexamethyleneamine hydrochloride zinc chloride*, $C_6H_{12}N_4,HCl,ZnCl_2$, groups of needle-shaped crystals; and *hexamethyleneamine hydrochloride cadmium chloride*, $C_6H_{12}N_4,HCl,CdCl_2 + H_2O$, monoclinic prisms almost insoluble in cold water.

Bismuth, antimony, and zinc chlorides give crystalline precipitates

with the base in hydrochloric acid solution, which are at once decomposed by water with formation of basic salts. A. W. C.

Silver Derivative of Guanidine. By JOHANNES THIELE (*Annalen*, 1898, **302**, 334).—The *silver* derivative, $CH_3N_3Ag_2$, is obtained as a white, flocculent precipitate, containing $1H_2O$, when baryta is added to a mixture of guanidine and silver nitrates in molecular proportion.
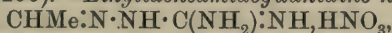M. O. F.

Preparation of Amidoguanidine. By JOHANNES THIELE (*Annalen*, 1898, **302**, 332—334. Compare Abstr., 1892, 1296).—Moderately dilute solutions of amidoguanidine salts, when treated with sodium hydrogen or potassium hydrogen carbonate, yield *amidoguanidine hydrogen carbonate*, $NH_2 \cdot NH \cdot C(NH) \cdot NH_2, H_2CO_3$, which is practically insoluble in cold water, and melts and decomposes at 172°; boiling water dissolves it in part, but also eliminates carbonic anhydride and ammonia. Although caustic alkalis remove carbonic anhydride, ammonia is without action on the substance, which is also formed when ammonium carbonate is added to an amidoguanidine salt, ammonia being eliminated.

In view of the fact that guanidine salts do not yield a precipitate with alkali hydrogen carbonates, the formation of a sparingly soluble salt with amidoguanidine may be utilised in the preparation of this compound. M. O. F.

Condensation of Amidoguanidine with Aliphatic Aldehydes and Ketones. By JOHANNES THIELE and EDUARD DRALLE (*Annalen*, 1898, **302**, 275—299).—*Ethylideneamidoguanidine nitrate*,
$$CHMe:N \cdot NH \cdot C(NH_2):NH, HNO_3,$$
separates in small prisms when a solution of amidoguanidine nitrate is treated with aldehyde, and allowed to evaporate over sulphuric acid; it melts at 144°, and gradually reduces ammoniacal silver nitrate. The hydrochloride and the free base are very unstable, and have not been isolated.
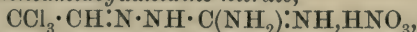
*Trichlorethylideneamidoguanidine nitrate*,
$$CCl_3 \cdot CH:N \cdot NH \cdot C(NH_2):NH, HNO_3,$$
crystallises in prisms containing $1H_2O$; it melts and decomposes at 113°, and yields amidoguanidineglyoxylic acid when the aqueous solution is boiled. The *hydrochloride* forms beautiful plates containing $2H_2O$; it melts at 83—84°, and decomposes at 110°.

Amidoguanidineglyoxylic acid, $NH:C(NH_2) \cdot NH \cdot N:CH \cdot COOH$, produced in the manner indicated, contains $1H_2O$, and melts and decomposes at 150—157°, according to the rate at which it is heated; the *hydrochloride* and *nitrate*, each containing $1H_2O$, melt and decompose at 197° and 182° respectively, whilst the *sulphate* crystallises in silky leaflets melting and decomposing at 136—137°. The *calcium*, *barium*, and *silver* salts each contain $1H_2O$, and the *methylic* salt, which melts and decomposes at 187—188°, forms a *hydrochloride* which contains $\frac{1}{2}H_2O$, and melts at 106—108°; in the anhydrous condition, the last-named substance melts at 110°, and decomposes at 160°. Reduction with tin and hydrochloric acid converts amidoguanidineglyoxylic acid into the *base*, $C_3N_4H_6O$, which forms a sparingly soluble *nitrate* melting at 308°.

Glyoxalbisamidoguanidine, $C_2H_2[:N \cdot NH \cdot C(NH_2):NH]_2$, is sparingly soluble in cold water, forming a yellow, alkaline solution in hot water; it crystallises in elongated, yellowish leaflets containing $1H_2O$, which melt and decompose at 265—266°. The *nitrate* is prepared by boiling an aqueous solution of amidoguanidine hydrochloride with excess of dichloraldehyde, and treating the liquid with nitric acid; it crystallises in white leaflets, and melts and decomposes at 292°. The *hydrochloride* forms long needles melting at 277°, and the *platinochloride*, which is sparingly soluble in water, crystallises in golden yellow needles; the *sulphate* contains $4H_2O$ and melts at 280—281°; the *dichromate* forms red, microscopic prisms, and the *nitrite* melts at 211°.
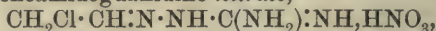
Chlorethylideneamidoguanidine *nitrate*,
$$CH_2Cl \cdot CH:N \cdot NH \cdot C(NH_2):NH, HNO_3,$$
forms crystals resembling ammonium chloride, and melts and decomposes at 144°; glyoxalbisamidoguanidine nitrate is produced on boiling the aqueous solution.
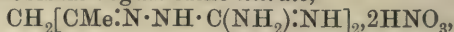
Diacetylbisamidoguanidine, $C_2Me_2[:N \cdot NH \cdot C(NH_2):NH]_2$, forming small, yellow crystals, melts and decomposes at 248—249°; the *hydrochloride* crystallises in long needles containing $2H_2O$, and melts at 308°. The *nitrate* becomes brown at 240°, without undergoing fusion, and the platinochloride forms needles containing $2H_2O$.

Dihydroxytartarobisamidoguanidine,
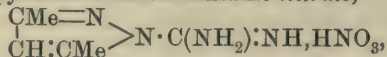$$(COOH)_2C_2[:N \cdot NH \cdot C(NH_2):NH]_2,$$
prepared from amidoguanidine hydrochloride and sodium dihydroxytartrate, is a white precipitate which contains $2H_2O$, and resembles starch; it becomes brown at 230°, but does not melt. The *hydrochloride* contains $2H_2O$, and melts and decomposes at 235°; the *calcium* salt forms white needles containing $4H_2O$, and the *silver* salt contains $2H_2O$.

Acetylacetonebisamidoguanidine *nitrate*,
$$CH_2[CMe:N \cdot NH \cdot C(NH_2):NH]_2, 2HNO_3,$$
gradually separates in large, rhombic crystals when acetylacetone is added to an aqueous solution of amidoguanidine nitrate (2 mols.); it slowly reduces an ammoniacal solution of silver nitrate, and melts at 197—199°. When the aqueous solution is boiled for several hours, amidoguanidine nitrate is eliminated, and dimethylpyrazolecarbonamidine nitrate produced.

3 : 5-Dimethylpyrazole-1-carbonamidine *nitrate*,
$$\begin{matrix} CMe = N \\ | \\ CH:CMe \end{matrix} \Big> N \cdot C(NH_2):NH, HNO_3,$$
crystallises from alcohol in white needles which melt and effervesce at 168°; boiling caustic soda in a reflux apparatus converts it into 3 : 5-dimethylpyrazole, which melts at 106—107°.

Acetonylacetonebisamidoguanidine, $C_2H_4[CMe:N \cdot NH \cdot C(NH_2):NH]_2$, crystallises from water in small, yellow prisms, which melt and effervesce at 224—225°; the *nitrate* melts at 239—240°, and the *hydrochloride*, which contains $2H_2O$, melts at 256—258°. The *platinochloride* forms yellow, microscopic needles, and contains $2H_2O$.

The *base*, $C_7H_{12}N_4$, is produced when amidoguanidine hydrochloride and acetonylacetone, in molecular proportion, are heated with alcohol

and a little water for 2½ hours in a reflux apparatus; it melts at 151°, and is so stable towards hydrolytic agents as to render it probable that the substance is a cyclic compound. The *hydrochloride* and *nitrate* melt at 244—245° and 188° respectively. M. O. F.

Diazoacetonitrile. By Theodor Curtius (*Ber.*, 1898, **31**, 2489—2492).—When methyleneamidoacetonitrile is treated with alcoholic normal hydrochloric acid, the salt of amidoacetonitrile is produced (Jay and Curtius, Abstr., 1894, i, 162), but if a saturated alcoholic solution of hydrogen chloride is used, *glycineamidoether dihydrochloride*, $NH_2 \cdot CH_2 \cdot C(OEt)\!:\!NH,2HCl$, is obtained; it is hygroscopic, and melts, evolving gas, at 170—188°. Nitrous acid converts it into ethylic diazoacetate.

Diazoacetonitrile, $N_2\!:\!CH \cdot CN$, obtained by the action of nitrous acid on amidoacetonitrile, is a limpid, orange-yellow liquid, having, when freshly prepared, the odour of acetonitrile, but rapidly becoming pungent; it boils at 46·5° under a pressure of 14—15 mm., and does not solidify at − 18°. It dissolves in water, and is much less stable than ethylic diazoacetate, being also more volatile than this substance in the vapour of ether. It explodes when brought into contact with copper oxide at the ordinary temperature. M. O. F.

Tetracetylhydrazide and Derivatives of Urazole. By Gerolamo Cuneo (*Chem. Centr.*, 1898, i, 38—39; from *Ann. Chim. Farm.*, 1897, **26**, 481—490).—By the action of methylic iodide on urazole at 120°, *methylurazole* and *dimethylurazole* are obtained; the former crystallises from water in small needles, is insoluble in chloroform, and melts at 216°, the latter crystallises from chloroform, in which it is easily soluble, and melts at 167°. Attempts to introduce another methyl group failed. *Diacetylurazole* prepared by heating 1 part of urazole with 6 parts of acetic anhydride for half-an-hour, crystallises from alcohol in white leaflets, is insoluble in ether, and melts at 206°; when boiled with water, it yields *acetylurazole*, which crystallises from water in colourless crystals, and melts at 221·5°. *Triacetylurazole* is obtained by heating diacetylurazole with 6 times its weight of acetic anhydride for 5 hours, and evaporating the solution in a vacuum over lime; it crystallises from anhydrous benzene in prisms, melts at 138°, is decomposed by the prolonged action of boiling acetic anhydride with formation of acetamide, and, when boiled with water, yields diacetylurazole. *Acetylphenylurazole*, prepared by boiling phenylurazole with twice its weight of acetic anhydride, crystallises from benzene in leaflets, and melts at 175°. *Diacetylphenylurazole* is obtained by boiling the monacetyl derivative with 4 times its weight of acetic anhydride for 3 hours, and evaporating the solution in a vacuum over lime; it crystallises from benzene in white needles, and melts at 164°. When urazole is heated with acetic anhydride and sodium acetate for 3 hours, carbonic anhydride is liberated and *tetracetylhydrazide*, $(C_2H_3O)_4N_2$, is formed; the latter, which may also be obtained by the action of acetic anhydride on hydrazine hydrate, melts at 86°, and crystallises from alcohol in long, rhombic crystals.

E. W. W.

Derivatives of Monochloracetoxime. By GEORG MATTHAI-
OPOULOS (*Ber.*, 1898, **31**, 2396—2399. Compare Abstr., 1896, i, 520).
—Chloracetoxime, when treated with alkalis, loses chlorine, but no
definite compound is formed.

Chloracetoximephenylcarbamide, produced by adding phenylcarbimide
to a solution of the oxime in benzene, crystallises from this solvent,
melts at 112°, and decomposes and evolves gas at 150—160°.

Triacetonylaminetrioxime, $N(CH_2 \cdot CMe:NOH)_3$, which is formed by
the action of dry ammonia on an ethereal solution of chloracetoxime,
melts at 184·5°, is soluble in hot water and alcohol, insoluble in ether,
reduces silver nitrate, and dissolves in alkaline solutions, from which it
is reprecipitated by carbonic anhydride.

The *methiodide* of the trioxime, $N(CH_2 \cdot C \cdot Me:NOH)_3$,MeI, produced
by warming the base with excess of methylic iodide, crystallises from
alcohol, and melts and decomposes at 231°. The *ethiodide* is produced
with greater difficulty and decomposes at 236°.

Piperidylacetoxime, $C_5H_{10}N \cdot CH_2 \cdot CMe:NOH$, produced from the
monochloroxime and piperidine in ethereal solution, crystallises from
alcohol in lustrous, white crystals and melts at 123°; it reduces silver
nitrate.   · G. T. M.

Condensation Products of Isobutaldehyde. By ADOLF FRANKE
and LEOPOLD KOHN (*Monatsh.*, 1898, **19**, 354—375).—The results
previously obtained by the authors in conjunction with Brauchbar
(Abstr., 1896, i, 404 ; 1897, i, 137 ; 1898, i, 353), are as follows. (1)
Pure isobutaldehyde, obtained by the depolymerisation of paraisobut-
aldehyde by Fossek's method, reacts with alcoholic potash (1 mol. to 3
mols. of the aldehyde), yielding isobutyric acid, a small quantity of
the hydroxy-acid, $CHMe_2 \cdot CH(OH) \cdot CMe_2 \cdot COOH$, and the octylglycol,
2 : 2 : 4-trimethylpentan-1 : 3-diol, $CHMe_2 \cdot CH(OH) \cdot CMe_2 \cdot CH_2 \cdot OH$. (2)
The only product obtained by the action of a small quantity of
alcoholic soda or potash at low temperatures ($-20°$) is isobutaldol.
(3) The same product may be obtained by allowing the aldehyde to
remain in contact with concentrated potassium carbonate solution for
some time at the ordinary temperature. (4) Aqueous potassium
hydroxide yields the aldol, glycol, and isobutyric acid. (5) When the
aldehyde is heated with sodium acetate in sealed tubes, the products
are Fossek's compound, $C_8H_{14}O$, and the octylglycol isobutyrate,
$CHMe_2 \cdot CH(OH) \cdot CMe_2 \cdot CH_2 \cdot O \cdot CO \cdot CHMe_2$. As these results do not
agree with those obtained by different authorities, namely, Pfeiffer
(*Ber.*, 1872, **5**, 699), Urech (Abstr., 1879, 520 ; 1880, 103, 538, 620),
Fossek (Abstr., 1882, 1279 ; 1884, 37), Perkin, jun. (Trans., 1883, **43**,
90), and Urbain (Abstr., 1896, i, 590), the authors have repeated the
whole of the experiments described by these different authorities.
They cannot corroborate Pfeiffer's statements, but confirm the results
obtained by Brauchbar (Abstr., 1897, i, 137). They also dispute
Urich's statement that a compound boiling at 154—157° can be
obtained by the action of potassium carbonate on the aldehyde ; they
find that solid potassium carbonate in the cold yields the aldol, but, on
boiling, the unaltered aldehyde is obtained, as at this temperature the
aldol is re-converted into the aldehyde.

Fossek's results, obtained by the action of sodium acetate solution on the aldehyde, are confirmed. The products are an oil boiling at 150°, the glycol isobutyrate (see above), and, under certain conditions, a third condensation product boiling at 200°. The formation of three neutral products as mentioned by Urban by the action of warm alcoholic soda has not been confirmed. The chief product is a mixture of the octylglycol and its isobutyrate. On repeating Perkin's work, the authors find that results similar to Perkin's can only be obtained by using isobutaldehyde which has not been purified by conversion into its polymeric form. With an impure aldehyde not thus purified, a fraction boiling at 153—157° is obtained. This oil yields an *oxime*, $C_7H_{12}{:}N{\cdot}OH$, and thus indicates that the original oil is $C_7H_{12}O$; it cannot be an aldehyde, since it is not oxidised on exposure to the air, its oxime gives no nitrile when treated with acetic anhydride, and it gives the iodoform reaction. All the facts indicate that the compound is a condensation product of isobutaldehyde and acetone, namely, $CHMe_2{\cdot}CH{:}CH{\cdot}COMe$. This constitution has been established by the actual synthesis of the compound from *pure* isobutaldehyde and acetone by using Perkin's condensation method; all the other fractions mentioned by Perkin were obtained in this condensation, and it is thus obvious that the aldehyde employed by Perkin must have contained acetone. J. J. S.

Synthesis of r-Glyceraldehyde. By A. WOHL (*Ber.*, 1898, **31**, 2394—2395. Compare Abstr., 1898, i, 555).—*r-Glyceraldehyde*, obtained by the hydrolysis of the corresponding acetal with decinormal sulphuric acid, is a white, crystalline powder having a sweetish taste and melting at 132°; it reduces silver nitrate in the cold. The molecular weight determination obtained by the freezing point method, in a freshly prepared solution, corresponds with 164, and only after two days does the number obtained, namely 90, agree with that of the simple molecule. This may be due to the fact that the compound in the solid state is bimolecular, and when dissolved only gradually changes, to the monomolecular condition. G. T. M.

Derivatives of Diacetyl. By HARRY F. KELLER and PHILIPP MAAS (*Chem. Centr.*, 1898, i, 23—24; from *J. Franklin Inst.*, 1897, **144**, 379—385).—By the action of cold hydrogen peroxide on di-bromodiacetyl, a solution of bromacetic acid is formed which, on heating, decomposes into hydrogen bromide and glycollic acid. Amongst the mixture of acids obtained by the action of hot nitric acid on di-bromodiacetyl, oxalic and bromacetic acids were detected. By the action of hydrogen peroxide on tetrabromodiacetyl, dibromacetic acid is not formed, but 30—40 per cent. of *pentabromacetone* is obtained, partly as a white, flocculent precipitate and partly in crystals which gradually separate from the solution. It crystallises from ether in long, colourless prisms which have a silky lustre, and from glacial acetic acid on addition of water in long, slender needles; it is insoluble in water, but very easily soluble in the ordinary organic solvents, has a peculiar penetrating odour, melts at 72·8°, and sublimes without apparent decomposition at a higher temperature. From the

mother liquor of the pentabromacetone, a small quantity of an oil, probably tribromacetone, was extracted with ether; it has a pungent odour and decomposes on heating. Tetrabromodiacetyl is not attacked even by fuming nitric acid.

Diacetylcyanhydrin, prepared by gently heating a mixture of di-acetyl with a 30 per cent. solution of hydrogen cyanide, is a colourless oil which cannot be crystallised; attempts to convert it into the corresponding acid also failed. *Dibromodiacetyldicyanhydrin* crystal-lises from ether in lustrous crystals and melts and decomposes at 177°; small quantities of the corresponding *acid amide* were obtained. *Tetrabromodiacetyldicyanhydrin* resembles the corresponding chlorine derivative. Attempts to prepare tetrachlorodiacetyl by the action of chlorine on diacetyl dissolved in carbon bisulphide or chloroform yielded only *dichlorodiacetyl*, which is very similar to dibromodiacetyl, crystallises in yellowish scales, melts at 124·5°, and is soluble in carbon bisulphide, chloroform, boiling light petroleum, and warm benzene.   E. W. W.

Chloralacetones. By L. GIGLI (*Gazzetta*, 1898, **28**, ii, 83—86).— A mixture of acetylacetone and anhydrous chloral gradually solidifies to a mass of *acetylacetonechloral*, $CCl_3 \cdot CH(OH) \cdot CH_2 \cdot C(OH)\!:\!CH \cdot COMe$; it crystallises in lustrous prisms melting at 78—79°.

Benzoylacetonechloral, $CCl_3 \cdot CH(OH) \cdot CH_2 \cdot CO \cdot CH_2 \cdot COPh$, is similarly obtained from benzoylacetone, and forms large, vitreous crystals melt-ing at 101—104°.

Benzoylacetonoximechloral, $CCl_3 \cdot CH(OH) \cdot CH_2 \cdot C(NOH) \cdot CH\!:\!CHPh$, prepared by the direct combination of chloral with benzoylaceton-oxime, forms lustrous crystals melting at 113—114°.   W. J. P.

Electrolysis of the Sodium Salts of Halogen-substituted Fatty Acids. By JULIUS TROEGER and E. EWERS (*J. pr. Chem.*, 1898, [ii], **58**, 121—128).—The electrodes consisted of spirally rolled platinum foil, the cathode being placed in a small, porous cell, and the whole apparatus kept cool with ice; the E. M. F. employed was 16 volts, the current about 0·5 ampère. In the case of sodium α-di-chloropropionate, an oily product was obtained at the anode; it solidified, but did not melt when heated, subliming instead; it is an unstable substance, and appears to be *α-dichlorethylic α-dichloropro-pionate*, $CMeCl_2 \cdot COO \cdot CMeCl_2$ (compare Elbs and Kratz, Abstr., 1897, i, 553). With sodium dichloracetate, a similar product seems to be formed, but it is even more unstable, hydrochloric acid and carbonic oxide being formed at the anode. With sodium chloracetate, no oily product was obtained. With sodium β-iodopropionate, iodoform was obtained at the anode.   C. F. B.

Manufacture and Applications of Lactic Acid. By ALAN A. CLAFLIN (*J. Soc. Chem. Ind.*, 1897, **16**, 516—518).—In order to deter-mine its complete decomposition by the lactic acid bacillus, the solu-tion of dextrose should have a sp. gr. ranging between 1·05 and 1·075; it seems advantageous if 10—15 per cent. of the saccharine matter consists of cane-sugar. The amount of nitrogen needed for the

growth of the ferment is about 2 per cent. of the weight of sugar employed, and is best added in the form of the extract obtained by treating bran with boiling water and dilute acid. The fermentation, which should take place at 45°, is best started by means of a pure culture of the lactic acid bacillus obtained during a previous fermentation ; to prevent butyric fermentation, the acidity must be rigidly confined between 0·02 and 0·5 per cent. by adding chalk or milk of lime. In from 3—6 days, the fermentation is completed, over 98 per cent. of the sugar being converted into lactic acid ; the ferment is then destroyed by heating to 100°, the solution evaporated, and the calcium lactate purified by recrystallisation. The free acid is obtained in a pure state by decomposing the aqueous calcium lactate with sulphuric acid, removing any excess of the latter by means of baryta, and evaporating the solution until it contains about 50 per cent. of lactic acid ; little of the latter is lost during evaporation, although about 7 per cent. is converted into lactic anhydride. W. A. D.

Lichenostearic Acid. By HUGO SINNHOLD (*Arch. Pharm.*, 1898, **236**, 504—522).—As the observations of previous workers on lichenostearic acid (from Iceland moss, "*Cetraria Islandica*") are not in accord, the author has submitted the acid to a further investigation (compare Hesse, Abstr., 1898, i, 534). For the preparation of the acid, the moss was extracted with ether, and, after evaporation of the solvent, the dark green residue was purified by treatment first with alcohol and then with light petroleum, in which the acid is insoluble.

Lichenostearic acid, $C_{18}H_{31} \cdot COOH$, crystallises from dilute alcohol in nacreous tetragonal or rhombic plates, melts at 124·5—125°, and resoldifies at 120—122°; it does not contain nitrogen, is almost tasteless, and is not acted on by bromine or potassium permanganate. The *potassium* and *ammonium* salts are crystalline, and the *silver*, *copper*, *calcium*, and *barium* salts are amorphous. The *methylic* salt separates from alcohol in colourless, flat prisms melting at 96—97°, and the *ethylic* salt crystallises with difficulty and melts at 60°.

Lichenosterylic acid, $C_{17}H_{33}O \cdot COOH$, obtained from the above acid by boiling for some hours with a 10 per cent. solution of potassium hydroxide, crystallises from alcohol in broad, rhombic leaflets melting at 83·5—84°, and in its behaviour towards reagents resembles the parent substance. The *silver* and *copper* salts are described. The acid is not acted on by sodium amalgam, and when heated with amorphous phosphorus and hydriodic acid in sealed tubes at 220—250°, is converted into an oil containing phosphorus.

The constitution of these acids remains doubtful, the want of material rendering further experiments impossible. A. W. C.

Preparation of Glyceric Acid. By ZINNO (*Chem. Centr.*, 1898, i, 26 ; from *Pharm. Centr.-H.*, **38**, 780).—The author prepares glyceric acid by adding nitric acid drop by drop to a hot mixture of 200 grams of glycerol, 200 grams of water, and 100 grams of red lead, which is kept stirred and not heated to above 100°. When the whole of the red lead is decolorised, the liquid is filtered through a hot filter, the residue washed with hot water, the filtrate concentrated in the steam bath, and then stirred with a slight excess

of sulphuric acid of sp. gr. $= 1\cdot53$.   The filtrate from the lead sulphate, after treatment with barium hydroxide and filtering, is finally concentrated in a vacuum over sulphuric acid, and any precipitated barium nitrate filtered off.   E. W. W.

Preparation of Amides. By OSSIAN ASCHAN (*Ber.*, 1898, **31**, 2344—2350).—Amides of organic acids have been hitherto obtained either by distillation of the corresponding ammonium salts, by decomposition of the alkylic salts with ammonia, or by the action of ammonia or ammonium carbonate on the acid chlorides.   Hofmann made use of a modification of the first method, which consisted in heating the ammonium salts under pressure at 230°.

The mixture of acid chloride and phosphorus oxychloride obtained on treating the organic acid with phosphorus pentachloride, when added to well cooled ammonia, yields the amide, but although this method renders the isolation of the chloride unnecessary, it has its disadvantages.   The phosphorus oxychloride always produces a certain amount of nitrile, and, moreover, the additional quantity of ammonia necessary to decompose the phosphorus compound is three times that required to form the amide.

Instead of phosphorus pentachloride, the author treats the acid with a slight excess of the trichloride, and the action is accelerated by warming; the mixture is then cooled in ice, and the organic chloride, decanted from the viscid phosphorous acid, is slowly added to a cooled solution of ammonia (25—28 per cent.).   The amide thus produced is isolated by suitable means, depending on the nature of the compound.   The amides of acetic, propionic, butyric, isobutyric, isovaleric, isocapric, oenanthylic, caprylic, stearic, oleic and sebacic acids are readily obtained by this method, and the following are described for the first time.

Undecylenamide crystallises from dilute alcohol, and melts at $84\cdot5$—$85\cdot5°$; it possesses a characteristic odour.

Suberamide, obtained by heating suberic acid with phosphorus trichloride, and decomposing the chloride in the usual way, crystallises from water in ill-defined prisms, sinters at 215°, and melts at 216—217°.   G. T. M.

Urethanes. By JOHANNES THIELE and FRANKLAND DENT (*Annalen*, 1898, **302**, 245—272. Compare Thiele and Lachmann, Abstr., 1896, i, 207).—*Methylic nitrocarbamate*, $NO_2\cdot NH\cdot COOMe$, prepared by treating a solution of methylic carbamate in sulphuric acid with ethylic nitrate at $-5°$, forms colourless, lustrous plates or monoclinic prisms, and melts at 88°; it decomposes at 120—130°, and yields methylic phenylcarbamate or diphenylcarbamide with warm aniline.   The *ammonium* derivative crystallises from warm water in colourless needles, and the *potassium* derivative forms large prisms; the *mercury* and *silver* derivatives crystallise in small needles.

Methylic nitrosocarbamate, $NO\cdot NH\cdot COOMe$, obtained by reducing methylic nitrocarbamate with zinc dust and glacial acetic acid, crystallises in yellow needles from a concentrated solution in ether to which petroleum has been added; it melts and decomposes at 61°.   The

ammonium derivative melts and decomposes at 105°; the *silver* derivative decomposes quickly in light. Water, dilute sulphuric acid, and aqueous mellitic acid eliminate nitrogen from the ethereal salt, the gas being accompanied by carbonic anhydride in the case of the agent last named; sulphuric acid also gives rise to methyl hydrogen sulphate, but no trace of ethyl hydrogen sulphate is obtainable from ethylic nitrosocarbamate under the same conditions. The authors regard it as possible that methylene is the initial product in the decomposition of methylic nitrosocarbamate, and in order to give support to this view, they have studied the behaviour of nitrosourethane towards dilute sulphuric acid in presence of bromine, and also the action of water and dilute acids on ethylic chlorocarbonate; in the first case, ethylenic bromide, and in the second case, ethylene, are formed, and no trace of ethylidenic derivatives.

Benzylic chlorocarbonate, $Cl \cdot COO \cdot CH_2Ph$, obtained on adding benzylic alcohol drop by drop to its own weight of carbonylic chloride at $-8°$, is a colourless oil with penetrating odour; it boils, and in part decomposes at 103°, under a pressure of 19—20 mm., and at 155° is completely resolved into carbonic anhydride and benzylic chloride. Ammonia converts it into benzylic carbamate.

Paranitrobenzylic chlorocarbonate, $Cl \cdot COO \cdot CH_2 \cdot C_6H_4 \cdot NO_2$, prepared by the action of carbonylic chloride on paranitrobenzylic alcohol, crystallises from light petroleum in colourless needles, and melts at 32°; the substance is resolved into carbonic anhydride and paranitrobenzylic chloride when heated. *Paranitrobenzylic carbamate*,
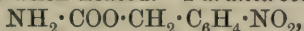
$$NH_2 \cdot COO \cdot CH_2 \cdot C_6H_4 \cdot NO_2,$$

obtained by treating the foregoing compound with ammonia, crystallises from benzene in pale yellow leaflets melting at 154°. *Paranitrobenzylic nitrocarbamate*, $NO_2 \cdot NH \cdot COO \cdot CH_2 \cdot C_6H_4 \cdot NO_2$, formed by the action of ethylic nitrate on paranitrobenzylic carbamate dissolved in sulphuric acid, crystallises from benzene in pale yellow needles and melts at 140°. The *ammonium* derivative crystallises in yellow plates and needles which melt and decompose at 153°; the *potassium* derivative forms prisms, the *mercury* derivative is amorphous, and the *silver* derivative crystallises in needles which resist the action of light. The *aniline* derivative separates from benzene in lustrous, monosymmetric plates, and melts and decomposes at 147°; the action of heat resolves it into nitrous oxide and *paranitrobenzylic phenylcarbamate*, $NHPh \cdot COO \cdot C_6H_4 \cdot NO_2$, which crystallises from alcohol in long, colourless needles and melts at 123°.

The *chlorocarbonate* of ethylic glycollate, $Cl \cdot COO \cdot CH_2 \cdot COOEt$, obtained by the action of carbonylic chloride on ethylic glycollate at 60° in sealed tubes, is a liquid of penetrating odour, which boils at 113° and 182—183° under pressures of 80 mm. and 714 mm. respectively, undergoing slight decomposition at the higher temperature. The *carbamate* of ethylic glycollate, $NH_2 \cdot COO \cdot CH_2 \cdot COOEt$, produced by treatment with ammonia, crystallises from benzene in large prisms and melts at 61°. The *nitrocarbamate*, $NO_2 \cdot NH \cdot COO \cdot CH_2 \cdot COOEt$, prepared by the action of ethylic nitrate on the carbamate dissolved in sulphuric acid, crystallises from benzene in slender, colourless leaflets and melts at 80°; the *silver* derivative crystallises from hot

water in transparent leaflets, and the *potassium* derivative forms small needles.

The *chlorocarbonate* of ethylic lactate, $Cl \cdot COO \cdot CHMe \cdot COOEt$, is a liquid of penetrating odour which boils at 91° and at 180°, under pressures of 19 mm. and 714 mm. respectively; ammonia converts it into the *carbamate*, $NH_2 \cdot COO \cdot CHMe \cdot COOEt$, which crystallises from benzene in attenuated leaflets, and melts at 65·5°. The *nitrocarbamate*, $NO_2 \cdot NH \cdot COO \cdot CHMe \cdot COOEt$, separates from benzene in small, mono-symmetric plates, and melts at 68°; the *silver* derivative forms large prisms and decomposes at 50°.

The urethanes of fatty alcohols, excepting methylic carbamate, yield olefines under the influence of nitrous acid, which decomposes them on the principle of the following equation, $2NH_2 \cdot COOEt + 2HNO_2 = 2CO_2 + 2N_2 + C_2H_5 \cdot OH + C_2H_4 + 3H_2O$. This reaction has been studied in the case of the urethanes derived from ethylic, propylic, isopropylic, and isobutylic alcohols. Benzylic and paranitrobenzylic carbamates yield the respective alcohols along with nitrogen and carbonic anhydride; allylic carbamate and the carbamates of ethylic glycollate and ethylic lactate also fail to yield unsaturated hydrocarbons.   M. O. F.

ψ-**Carbamides.** By ERNST SCHMIDT (*Arch. Pharm.*, 1898, **236**, 441—445. Compare next abstract).—The researches of Falke (*Diss. Marburg*, 1893), Gadamer (Abstr., 1896, i, 140, 414), and Schacht (Abstr., 1898, i, 12) have shown that thiocarbamide, thiosinamine (allylthiocarbamide), ethylenethiocarbamide, and trimethylenethiocarb-amide can exist in two tautomeric forms; the last two substances cannot, however, be directly converted into ψ-carbamides, as is the case with thiosinamine and other alkylated thiocarbamides.

The conversion of allylthiocarbamide into the ψ-form can be brought about, as Gabriel (Abstr., 1890, 127) has shown, by fuming hydro-bromic or hydrochloric acids at 100°, or (compare Gadamer) by the action of bromine or iodine at ordinary temperatures.

The bromopropylenecarbamide of Andreasch is shown by Rundqvist (compare next abstract) to be a bromine substitution product of Gabriel's ψ-allylcarbamide; especially is this shown by its synthesis from dibromopropylamine and potassium cyanate.

Diallylcarbamide (sinapoline) and diallylthiocarbamide are acted on by bromine and iodine with formation of ring compounds, namely, halogen substitution products of ψ-carbamides or ψ-thiocarbamides.
                                                                      A. W. C.

Allyl Substituted Carbamides and Thiocarbamides. By CARL RUNDQVIST (*Arch. Pharm.*, 1898, **236**, 445—447. Compare preceding abstract).—Thiosinamine dicyanide, first obtained by Maly (*J. pr. Chem.*, 1868, 413), is best prepared by passing cyanogen into an aqueous solution of thiosinamine; it crystallises from ethylic acetate in glistening, bronze-coloured, microscopic plates, and its alcoholic solution does not show any green fluorescence, as Maly has stated to be the case. It decomposes, without previously melting, when heated in a capillary tube to 193°, and gives precipitates with the salts of the heavy metals, but is not acted on by picric or phosphomolybdic acids.

When warmed with dilute sulphuric or hydrochloric acids, it is converted into allylthioparabanic acid; this crystallises in long, lemon-yellow needles, melts at 89°, and gives precipitates with platinic, mercuric, auric, and cupric chlorides, which are apparently not homogeneous but mixtures of several substances. With silver nitrate, a precipitate is formed which, on gently warming, is decomposed, sulphur being eliminated and silver allylparabanate formed.

Allyparabanic acid, obtained from the silver salt by the action of hydrogen sulphide, separates in transparent, glistening, needle-shaped crystals melting at 140° and is identical with the acid prepared by the action of allylic iodide on silver parabanate.

Allylthioparabanic acid is converted into potassium oxalate and thiosinamine by the action of potassium hydroxide, and in presence of sodium carbonate, to neutralise the nitric acid formed, silver nitrate converts it into allylcarbamide, melting at 85°, and oxalic acid. Maly (*loc. cit.*) gives the melting point of this substance as 141°, and the author concludes that Maly's compound must have been either silver oxalate (m. p. 140°) or a mixture of the decomposition products of allylcarbamide.

The allylcarbamide from which the following compounds were prepared was obtained by Andreasch's method, namely, the action of potassium isocyanate on allylamine sulphate. It is an oil which, on cooling, solidifies to a mass of radiating needles, melts at 85°, and resembles carbamide in its behaviour towards acids, but differs from it in not so readily forming salts and double salts.

Dibromopropylcarbamide, $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CHBr \cdot CH_2Br$, formed by the direct action of bromine on allylcarbamide, is a white, crystalline powder melting at 109°, and agrees in its properties with those ascribed to it by Andreasch (*Monatsh.*, **5**, 39), as do also bromo-ψ-allylcarbamide and its hydrobromide. The former gives an *aurichloride*, $C_4H_7BrN_2O,HAuCl_4$, separating in glistening, dark orange-red crystals melting at 120·5°, and a *picrate* crystallising in yellow needles and melting at 175°.

Iodo-ψ-allylcarbamide hydriodide, $C_4H_8N_2OI_2$, obtained by the action of a solution of iodine in potassium iodide on allylcarbamide, separates in well formed, transparent crystals melting and decomposing at 105—108°. Silver chloride converts it into the corresponding *hydrochloride*, forming thin, exceedingly soluble needles, melting at 111°. The *platinochloride* forms beautiful yellow crystals; the *aurichloride*, yellowish-red crystals melting at 140°, and the *picrate* transparent, yellowish-green needles melting at 159°. The *free base* obtained from the hydriodide by the action of potassium hydroxide, crystallises in glistening plates, and melts at 104—106° with separation of iodine.

Hydroxy-ψ-allylcarbamide was prepared from the iodine base by the action of silver nitrate, and identified as its *platinochloride* and *aurochloride*. The former, $(OH \cdot C_4H_7N_2O)_2, H_2PtCl_6$, crystallises in dark coloured, tetragonal leaflets, and the latter is a red-brown, oily liquid, solidifying to a mass of yellowish needles.

Bromo-ψ-allylcarbamide methiodide crystallises from methylic alcohol in glistening crystals, and by digestion with silver chloride is converted into the corresponding chloride, giving a *platinochloride*

which separates in orange crystals. *Iodo-ψ-allylthiocarbamide meth-iodide* separates from methylic alcohol in transparent, yellow crystals melting at 119°, and gives a *platinochloride* forming yellowish-red, glistening crystals.

Cyanogen has no action on allylcarbamide. When reduced with sodium amalgam or zinc and acetic acid, bromo-ψ-allylcarbamide, hydrobromide, or the corresponding iodine compound, is converted into allylcarbamide, so that these substances must have a constitution similar to that of thiosinamine bromide; this view is further supported by the synthesis of bromo-ψ-allylcarbamide from dibromopropylamine and potassium isocyanate.

Sinapoline (diallylcarbamide) is best prepared by Will's method (*Annalen*, 1844, **52**, 26). With platinic, auric, and mercuric chlorides, it gives amorphous precipitates, but nothing with picric or tannic acid. It is readily acted on by bromine, and from the product, after treatment with silver chloride, an *aurichloride* is obtained as a viscid mass, and a *picrate* as a fine, crystalline powder melting at 121°, which is a proof of the fact that, by the action of bromine, sinapoline undergoes a rearrangement, with formation of a ring compound. Iodine also combines with sinapoline at the ordinary temperature. Diallylthiocarbamide, prepared according to Hecht's directions (Abstr., 1890, 477), forms large, glistening leaflets melting at 49·5°, and behaves towards acids and the salts of heavy metals just as diallylcarbamide does. With bromine, it forms a dark coloured, syrupy bromide, which gives a precipitate with silver nitrate, proving that ring formation has taken place. After decomposition with silver chloride, it gives an aurochloride and platinochloride as amorphous precipitates which were not analysed. In its behaviour towards iodine, it fully resembles sinapoline, and does not yield a compound with cyanogen.   A. W. C.

Sulphonation of the Paraffins. By R. A. WORSTALL (*Amer. Chem. J.*, 1898, **20**, 664—675).—The results described below show that aliphatic as well as benzenoid hydrocarbons are capable of direct sulphonation; although cold fuming sulphuric acid is without action on hexane, heptane, and octane, it rapidly effects sulphonation when added to the hydrocarbons at their boiling points, monosulphonic acids being produced. Disulphonic acids are sometimes formed in small quantity under these conditions, but are prepared by passing sulphuric anhydride through the boiling paraffins.

Normal hexanesulphonic acid, prepared by adding successive small portions of fuming sulphuric acid to the boiling hydrocarbon, is a thick, light-brown liquid, which is very soluble in water and alcohol, but insoluble in ether; from 30—40 per cent. only of the theoretical quantity is obtained, the remainder of the hydrocarbon being completely oxidised. The barium salt, $(C_6H_{13}SO_3)_2Ba$, separates in brownish plates, and is extremely soluble in water, but insoluble in alcohol and ether, and the *lead* salt closely resembles it. *Normal hexanedisulphonic acid*, $C_6H_{12}(SO_3H)_2$, is a thick syrup, extremely soluble in water and very deliquescent; it is insoluble in light petroleum and ether, but soluble in hot benzene and alcohol. The

barium salt, $C_6H_{12}(SO_3)_2Ba$, is golden-yellow, very soluble in water, and very deliquescent; the *lead* salt, $C_6H_{12}(SO_3)_2Pb$, has similar properties.

From normal heptane, the same yield of monosulphonic acid is obtained as from normal hexane; the barium salt, $(C_7H_{15}SO_3)_2Ba$, the *lead* salt, $(C_7H_{15}SO_3)_2Pb$, and the free acid closely resemble the corresponding derivative of hexane, as also do *normal heptanedisulphonic acid*, $C_7H_{14}(SO_3H)_2$, its *barium* salt, $C_7H_{14}(SO_3)_2Ba$, and its *lead* salt, $C_7H_{14}(SO_3)_2Pb$, the derivatives which correspond with them.

Normal octanesulphonic acid, $C_8H_{17}SO_3H$, its *barium* salt, $(C_8H_{17}SO_3)_2Ba$, its *lead* salt, $(C_8H_{17}SO_3)_2Pb$, and *normal octanedisulphonic acid* closely resemble the corresponding derivatives of hexane and heptane.

On passing sulphuric anhydride into boiling hexane and heptane, there is formed, in each case, in addition to the disulphonic acid, a very small quantity of a brown, brittle *solid*, which is insoluble in water and all organic solvents; from normal octane, a considerable quantity of a similar substance is obtained. The analyses show that these compounds belong to a regular series, and their richness in oxygen suggests that they are possibly oxysulphones. W. A. D.

Aliphatic Sulphonic Acids. II. By ELMER P. KOHLER (*Amer. Chem. J.*, 1898, **20**, 680—695. Compare Abstr., 1898, i, 68).— *Ethylenesulphonic acid*, $CH_2\!:\!CH\cdot SO_3H$, is prepared by boiling $\alpha\beta$-ethanedisulphonic chloride with five times its weight of water until completely dissolved; the solution is evaporated until the whole of the hydrochloric acid formed has been removed, then neutralised with solid ammonium carbonate, and evaporated to dryness. After adding a small quantity of absolute alcohol and again evaporating to dryness, the residue is boiled with absolute alcohol and filtered; ammonium ethylenesulphonate dissolves in the alcohol, and is thus freed from ammonium ethanedisulphonate, which is insoluble. Ethylenesulphonic acid, obtained from its ammonium salt by boiling the latter with lead carbonate, decomposing the lead salt thus obtained with hydrogen sulphide, and evaporating on the water-bath, and over sulphuric acid, is an oily liquid which is very soluble in water, alcohol, and glacial acetic acid, but only sparingly in ether and chloroform. It is formed when $\alpha\beta$-bromethanesulphonic chloride is distilled under increased pressure, hydrogen bromide being evolved, and can be prepared by heating the acetyl derivative of potassium, sodium, or barium isethionate at 185°, acetic acid being also formed. *Ammonium ethylenesulphonate*, $CH_2\!:\!CH\cdot SO_3\cdot NH_4$, crystallises from dilute alcohol in large, orthorhombic plates, and from boiling absolute alcohol in short prisms; when heated, it melts completely at 156°, but immediately resolidifies; the *product* is colourless, reacts with bromine and potassium permanganate in the cold, evolves ammonia when heated with alkalis, and is decomposed when heated a few degrees above 156°. *Potassium ethylenesulphonate*, $C_2H_3SO_3K$, is very soluble in water, and crystallises from the latter in large plates, and from alcohol in slender needles; the *sodium* salt, $C_2H_3SO_3Na$, closely resembles it, whilst the *barium*

salt, $(C_2H_3SO_3)_2Ba + H_2O$, is insoluble in alcohol and crystallises from water in minute needles. The *lead* salt, $(C_2H_3SO_3)_2Pb + 2H_2O$, is only sparingly soluble in cold water, crystallises in hard, lustrous prisms, and, when heated, is decomposed after losing its water of crystallisation.

Ethylenesulphonic chloride, $CH_2\!:\!CH\!\cdot\!SO_2Cl$, prepared by the action of phosphorus pentachloride on the potassium salt suspended in chloroform, is an oily liquid which boils at 118—120°, with slight decomposition under a pressure of 250 mm., and is easily hydrolysed by boiling water.

Ethylenesulphonic acid is completely oxidised by a cold acid solution of potassium permanganate; in presence of alkali, the action is the same, but takes place more slowly, and the same is the case with all other oxidising agents.

Ethylenesulphonic acid is reduced only with difficulty; it is converted by sodium amalgam into isethionic acid, by the addition of the elements of water, but remains unacted on when boiled with zinc and dilute sulphuric acid during 24 hours. When, however, it is heated with hydriodic acid and phosphorus for 10 hours at 170°, it is converted into ethanesulphonic acid, isethionic acid being also formed.

Although ethylenesulphonic acid is not changed by boiling during 10 hours with water, it is converted into isethionic acid when boiled with dilute alkalis, or heated with water at 150° during several hours. The acid formed was identified by its sulphonic chloride, and yielded a potassium salt which melted at 190°, whereas Liebig has stated that potassium isethionate melts at 350°; on repeating the latter's experiments, however, a salt was obtained which melted at 190°.

Potassium $\alpha\beta$-chlorethanesulphonate is formed together with some isethionate, by heating potassium ethylenesulphonate during 5 hours at 130° with concentrated hydrochloric acid; hydrobromic acid, under the same conditions, gives rise to *potassium $\alpha\beta$-bromethanesulphonate*. The latter crystallises from water in orthorhombic plates, and from absolute alcohol in thin, friable laminæ; it is converted by silver oxide into potassium isethionate. The corresponding *sodium $\alpha\beta$-bromethanesulphonate* is prepared by adding sodium sulphite to ethylenic bromide dissolved in very dilute alcohol. Details concerning this will be published later.

Bromine acts by substitution on aqueous potassium ethylenesulphonate, *potassium bromethylenesulphonate*, $C_2H_2Br\!\cdot\!SO_3K$, being formed; this crystallises from boiling absolute alcohol in long, colourless needles, is extremely hygroscopic, and is very soluble in water. It is decomposed by dilute barium hydroxide, barium sulphite and bromide being formed; from the solution obtained, ether extracts a gum-like *substance*, which hardens in the air to a horn-like mass of varying composition. It is not changed by silver oxide, or by a cold solution of potassium permanganate, but is oxidised, when heated with the latter, to carbonic anhydride and water, whilst nitric acid gives rise, in addition, to a small quantity of oxalic acid. It appears probable, from the manner of its decomposition by barium hydroxide, that the potassium bromethylenesulphonate described above has the structure $CH_2\!:\!CBr\!\cdot\!SO_3K$.   W. A. D.

Acetylene Derivatives. By HUGO ERDMAN and PAUL KÖTHNER (*Zeit. anorg. Chem.*, 1898, **18**, 48—58).—When acetylene is passed over finely divided copper heated to 400—500°, it is decomposed into hydrogen and carbon, the latter being deposited in the graphitic condition. At lower temperatures (below 250°), the copper combines with the gas to form a yellowish-brown *compound*, which, unlike Söderbaum's cupric acetylide (Abstr., 1897, i, 309), is not explosive. The new substance is more conveniently prepared by heating finely divided cuprous oxide in a current of acetylene at 250°; it is exceedingly voluminous, and its composition corresponds with the formula $C_{44}H_{64}Cu_3$; when heated with excess of zinc dust, it yields 20 per cent. of an oil boiling between 190—250°, and possessing an odour like Caucasian naphtha; if the mixture is heated to a higher temperature, aromatic hydrocarbons appear in the distillate and naphthalene is obtained, whilst a portion which dissolves in caustic soda has properties resembling those of cresol.

It is difficult to obtain well defined acetylides of the metals of the potassium group. Rubidium, although acted on by acetylene at low temperatures, gives rise to no definite product. Zinc and mercury are scarcely acted on, and iron, like copper, acts catalytically, inducing condensation to oily hydrocarbons.

Solutions of thallium, lead, cadmium, iron, nickel, cobalt, platinum, iridium, and rhodium salts give no precipitate with acetylene; gold chloride gives a black precipitate, which, on warming, changes to metallic gold, palladium chloride gives a brown precipitate which is soluble in ammonia, in each case the precipitation being accompanied by the production of an aldehydic odour.

Copper acetate and silver nitrate yield brownish-red and white precipitates respectively.

Mercurocarbide nitrate, $HgC\!:\!CHg,HgNO_3 + H_2O$, produced by saturating a hot solution of mercuric nitrate with acetylene, separates in small, white crystals, and differs from Keiser's silver analogue, $C_2Ag_2,AgNO_3$, in containing H_2O. It resembles Poleck and Thümmel's mercury derivative of vinyl alcohol (Abstr., 1890, 118), and yields acetaldehyde on treatment with dilute acids.

Acetaldehyde is produced when acetylene is passed through a suspension of mercuric oxide in boiling phosphoric acid of sp. gr. = 1·15, or in 30 per cent. sulphuric acid.　　　　　　　　　　　　　　　G. T. M.

Action of Acetylene on Mercuric Nitrate. By PAUL KÖTHNER (*Ber.*, 1898, **31**, 2475).—Hofmann has recently (Abstr., 1898, i, 635) described a crystalline substance obtained by the action of acetylene on a solution of mercuric nitrate. The author had previously studied this compound, obtaining results similar to those of Hofmann, and had drawn attention to the relationship of the substance to vinylic alcohol and acetaldehyde (see Köthner, *Halle. a. S. Frühjahr*, 1896; and Erdmann and Köthner, preceding abstract).

The differences in the composition assigned to the substance by Hofmann and by the author may be due to a slight difference in the conditions of preparation, and the author states his intention of re-examining the question from this point of view.　　　　　　　　A. L.

A Compound of Acetylene with Cuprous Oxychloride. By
R. CHAVASTELON (*Compt. rend.*, 1898, 127, 68—69. Compare Abstr.,
1898, i, 613).—The crystalline compound of acetylene with cuprous
chloride, C_2H_2,Cu_2Cl_2, is decomposed by water, with production of a
violet compound ; acetylene is, at the same time, slowly liberated, and
the liquid is found to contain free hydrochloric acid, which limits the
decomposition. The violet substance is best prepared by digesting the
compound C_2H_2,Cu_2Cl_2 with a large excess of water, saturated with car-
bonic anhydride, out of contact with air. The crystals are washed with
absolute alcohol and anhydrous ether, and finally dried over calcium
chloride in an atmosphere of carbonic anhydride. Estimation of the
copper and chlorine, and the measurement of the volume of acetylene
which the compound yields when treated with concentrated hydro-
chloric acid, show that it has the composition C_2H_2,Cu_2Cl_2,Cu_2O.

N. L.

Combination of Carbon Compounds with Mercuric Sul-
phate. By GEORGES DENIGÈS (*Compt. rend.*, 1898, 126, 1868—1871).—
The carbon compounds capable of combining with mercuric sulphate in
acid solution (Abstr., 1898, i, 546) are thiophen and its derivatives,
the olefines, terpenes, and hydrocarbons of the benzene series and
their respective derivatives, aldehydes, and ketones ; they are all
characterised by the existence of latent valencies or the occurrence of
double bonds.

Acetone yields the calculated quantity of a white, crystalline com-
pound, $C_3H_6O,3HgO,2HgSO_4$, completely soluble in hydrochloric acid,
and its homologues of low molecular weight yield similar compounds,
but in the case of ketones of high molecular weights the reaction is
complex, condensations taking place and secondary products being
formed. When the compounds are suspended in water and treated
with hydrogen sulphide, the ketone is liberated.

Acetylacetone, pyruvic acid, acetonedicarboxylic acid, &c., yield
similar compounds, which will be described subsequently.

C. H. B.

Derivatives of the Naphthene or Cyclohexane Series. By
WLADIMIR B. MARKOWNIKOFF (*Annalen*, 1898, 302, 1—42. Compare
Abstr., 1898, i, 637 ; also von Baeyer, Abstr., 1894, i, 174).—The
author supplies an historical account of the information to be found on
the subject of hexanaphthene. By reducing the iodide which boils at
193°, with a copper–zinc couple in hydrochloric acid, the hydrocarbon is
obtained having the sp. gr. = 0·7902 at 0°/0°, or 0·7727 at 20°/0° ; it
boils at 80·5—81° under a pressure of 761·5 mm. Hexanaphthene has
an odour of pure " benzine," which is less penetrating than that of
petroleum ; it undergoes little change in contact with a mixture of
nitric and sulphuric acids at the ordinary temperature, but at 100° very
vigorous action takes place. The hydrocarbon is quite indifferent
towards cold fuming nitric acid, and even the boiling liquid acts
slowly, producing chiefly adipic acid.

Chlorohexanaphthene, $C_6H_{11}Cl$, is prepared by the action of moist
chlorine on the hydrocarbon in diffused light ; if the operation is con-

ducted with the dry gas, it is necessary to heat the liquid until it nearly boils, but the method is less satisfactory owing to the production of more heavily chlorinated derivatives. It is a colourless liquid, and is quite stable in the dry state, but becomes yellow and then brown when contaminated with water or with hydrogen chloride. The substance boils at 142° and 143° under pressures of 750 mm. and 768 mm. respectively; it has a sp. gr. = 0·990 at 0°/0° or 0·973 at 20°/0°. Boiling alcoholic potash converts it with difficulty into naphthylene and the ether C_6H_{11}·OEt.

Chloronaphthylene [*chlorocyclohexene*], C_6H_9Cl, obtained by the action of phosphorus pentachloride on ketohexamethylene, boils at 142—143°, and has an agreeable odour; it decolorises the vapour of bromine.

On fractionating the less volatile products of the action of chlorine on hexanaphthene, isomeric *dichloro*-derivatives are obtained. Two portions of the distillate boiling at 192—194° and 196—198° have the sp. gr. = 1·167 and 1·172 respectively at 15°/15°; the results of analysis agree with the requirements of the formula $C_6H_{10}Cl_2$.

Iodohexanaphthene boils at 193° under a pressure of 765 mm., decomposing slightly at that temperature; it is a pale yellow liquid, and quickly becomes coloured with iodine when exposed to light.

Bromine acts on hexanaphthene at 110° without producing a monobromo-derivative. When the halogen is employed in molecular proportion, upwards of half the hydrocarbon remains unchanged, the remainder being converted into polybromo-derivatives. In presence of aluminium bromide, a product derived from methylpentamethylene is obtained, and appears to be a mixture of the compounds $C_6H_4Br_8$ and $C_6H_3Br_7$; it melts at 120—121°, and is identical with the substance obtained by Kistner from methylpentamethylene (hexahydrobenzene), bromine, and aluminium bromide. This affords a new instance of conversion of the hexamethylene into the pentamethylene ring.

Nitrohexanaphthene, C_6H_{11}·NO_2, prepared by heating the hydrocarbon with nitric acid (sp. gr. = 1·075) at 115—120° during 10 hours, is a pale yellow liquid having an odour resembling that of nitrobenzene; when rapidly distilled under diminished pressure, it is colourless. The substance boils at 109° and 205·5—206° under pressures of 40 mm. and 768 mm. respectively; it has a sp. gr. = 1·0759 at 0°/0°, and 1·0616 at 20°/20°. Sodium ethoxide precipitates the *sodium* derivative in leaflets readily soluble in water; the solution develops an intense, reddish-brown coloration with ferric chloride, and yields, with lead acetate, a white precipitate which dissolves in excess of the agent.

The *compound* $C_{12}H_{20}(NO_2)_2$ remains in the distilling flask when crude nitrohexanaphthene is fractionated, and crystallises from light petroleum in white, lustrous plates; it decomposes when gradually heated, but if plunged into liquid at 200°, melts at 208—209°.

Hexanaphthene ketone (ketohexamethylene), $C_6H_{10}O$, prepared by heating nitrohexanaphthene with zinc dust and glacial acetic acid, is identical with the ketone obtained from hydroxyhexamethylene by von Baeyer (*loc. cit.*, 175), and yields adipic acid on oxidation. When the ketone, dissolved in a mixture of alcohol and ether, is reduced

with sodium, *naphthenol* or *hexanaphthenol* (hydroxyhexamethylene) is produced.

O-Naphtheneglycol, $C_6H_{10}(OH)_2$, obtained by the action of potassium permanganate on naphthylene, crystallises from ethylic acetate in lustrous scales, and melts at 99—100°; it sublimes slowly at 70°, and boils at 225° (uncorr.), when it undergoes partial decomposition.

Amidonaphthene or *amidohexanaphthene* (hexamethyleneamine), $C_6H_{11} \cdot NH_2$, a colourless liquid with a powerful odour of ammonia, is prepared by reducing nitrohexanaphthene with tin and hydrochloric acid; it boils at 134° under a pressure of 768 mm., and has the sp. gr. = 0·88216 at 0°/0°, and 0·86478 at 20°/0°. Derivatives of this base have been already described by von Baeyer (*loc. cit.*). The *hydrobromide* crystallises in elongated prisms, and yields a *platinobromide* and an *auribromide*. The *hydriodide*, *nitrate*, and *oxalate* crystallise in needles, and the *sulphate* forms leaflets.

Naphthylene or *hexanaphthylene* (*tetrahydrobenzene*, *cyclohexene*) prepared from the chloride by the action of quinoline or of alcoholic potash, boils at 83—84° under a pressure of 752 mm., and has a sp. gr. = 0·80893 at 0°/0°. The *dichloride*, $C_6H_{10}Cl_2$, boils at 187—189°.

The *hexaterpene*, C_6H_8, obtained from a hexanaphthylene dichloride which boils at 190—192°, has the penetrating odour of allylene, and is probably identical with von Baeyer's dihydrobenzene; it boils at 83—86° under a pressure of 767 mm., and has a sp. gr. = 0·8706 at 0°/0°, and 0·8531 at 20°/0°. One drop of the hydrocarbon develops an intense red coloration with a mixture of alcohol and concentrated sulphuric acid; the dibromide melts at 184°. An isomeric *hexaterpene*, prepared from the dichloride which boils at 196—198°, closely resembles the foregoing hydrocarbon; it boils at 83—86° under a pressure of 757 mm., and develops a deep violet-blue coloration with alcoholic sulphuric acid. Bromine converts it into an oily mixture, from which the dibromide melting at 184° crystallises. It is probable that this terpene has the constitution represented by the formula $CH_2 {\Large <} {\substack{CH:CH \\ CH:CH}} {\Large >} CH_2$, whilst the terpene which develops a red coloration has the unsymmetrical constitution represented by the formula

$$CH {\Large <} {\substack{CH-CH \\ CH_2 \cdot CH_2}} {\Large >} CH \quad \text{or} \quad CH {\Large <} {\substack{C==CH \\ CH_2 \cdot CH_2}} {\Large >} CH_2.$$
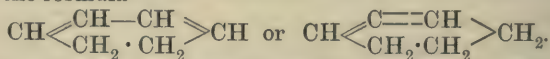
Examination of the crystalline dibromide has shown it to be a mixture, fractions having been obtained, on recrystallisation, melting variously between 184° and 192°.

Hexanaphthene is converted almost quantitatively into adipic acid when it is heated with nitric acid of sp. gr. = 1·235 in sealed tubes in a water bath; the hydrocarbon obtained from naphtha is an advantageous source of the acid. Iodonaphthene and chloronaphthene are converted into methylpentamethylene when heated with hydriodic acid, a small quantity of hexamethylene being also produced (compare Abstr., 1897, i, 402.

A useful summary of the general properties of hexanaphthene and its derivatives brings the paper to a conclusion.   M. O. F.

Stereoisomeric Oximes in the Hydroaromatic Series. By EMIL KNOEVENAGEL and J. GOLDSMITH (*Ber.*, 1898, **31**, 2465—2474).— The oxime of 3-phenyl-1-methylcyclohexenone-5 has been obtained by Werner (*Dissertation Heidelberg*, 1894), and by Bialon (*ibid.*, 1897), who describe it as melting at 115°; on the other hand, Jackson (*ibid.*, 1896) and Ruschhaupt (*ibid.*, 1897) obtained melting points of 151° and 152° respectively. Experiments made by the present authors show that the apparent discrepancy is due to the existence of two isomeric oximes, and that the character of the product obtained depends on the mode of preparation. The two substances may be separated, when admixed, by treatment with a mixture of alcohol and light petroleum in which the α-oxime (m. p. 115°) is much more readily soluble than the β-oxime (m. p. 151°). The crude product is obtained by the method of Werner or of Ruschhaupt, according as it is desired that a pre-dominance of the α- or the β-modification respectively shall be pro-duced. The former method consists in heating the ketone with a 10 per cent. solution of hydroxylamine hydrochloride in dilute alcohol on the water bath for an hour and a half; in the latter method, the ketone is dissolved in alcohol, mixed with an aqueous solution of sodium carbonate in excess, and then with solid hydroxylamine hydro-chloride, the alcohol being finally driven off on the water-bath.

Both oximes are optically inactive. The β-oxime crystallises in the tetragonal system, the axial ratio being $1 : 0.6706$.

The α-derivative is converted into the β-modification when its solution in warm acetic acid is evaporated under slightly reduced pressure; the reverse change is effected by dissolving the β-oxime in warm soda and reprecipitating it from the solution by neutralisation, and the same result may be achieved by careful sublimation of the β-oxime.

Both oximes yield the original ketone on hydrolysis with dilute sulphuric acid, and, on reduction with sodium and alcohol, yield the same 5-amido-3-phenyl-1-methylcyclohexane (compare Jackson, *loc. cit.*). The *hydrochloride* of this base separates from hot water in crystals melting at 235°, and dissolves in chloroform and alcohol, but is insoluble in ether and light petroleum. The *platinochloride* has the composition $(C_{13}H_{17}N), H_2PtCl_6$.

Experiments were made with a view of ascertaining if the ketone suffered any change under the influence of small quantities of alkali or acid, but without noteworthy result, and the authors conclude that the relationship between the two oximes is a stereoisomeric one. It is uncertain as yet, however, which of them is the *cis* and which the *trans* form, although a possible clue to the question is afforded by the behaviour of the two oximes towards phosphorus pentachloride, as only the β-oxime yields any product having the properties of a nitrile.

Phenylmethylcyclohexenone yields two stereoisomeric *semicarb-azones*, which may be separated by means of alcohol. One of these, the more sparingly soluble, melts at 199—200° but has not as yet been analysed; the other is obtained in the form of bundles of white needles melting at 170—171°, and has the composition $C_{14}H_{17}NO_3$.

A. L.

Formation of Suberone from Ecgonine. By RICHARD WILL-STÄTTER (*Ber.*, 1898, **31**, 2498—2508. Compare Abstr., 1893, i, 378, 713 ; 1894, i, 523).—Hydrotropilidinecarboxylic acid, prepared by the methylation of hydroecgonidine ethylic ether, is converted by reduction with sodium and amylic alcohol into cycloheptanecarboxylic acid, $C_7H_{13}\cdot COOH$, which is identical with the acid obtained by Einhorn and Willstätter by the reduction of tropilidinecarboxylic acid. This acid readily yields a monobromo-derivative, which, on treatment with baryta, is converted into Spiegel's a-hydroxycycloheptanecarboxylic acid, $OH\cdot C_7H_{12}\cdot COOH$ (Trans., 1881, 541), Δ^1-cycloheptenecarboxylic acid, $C_7H_{11}\cdot COOH$, being produced at the same time; the latter melts at 49—50°, and is identical with the Δ^1-ethylcyclopentenecarboxylic acid of Einhorn and Willstätter; this also has been prepared by Spiegel, and by Buchner and Jacobi (Abstr., 1898, i, 637). When a-hydroxycycloheptanecarboxylic acid is treated with lead peroxide, it is at once converted into suberone, 40 per cent. of the theoretical yield being obtained.

It thus appears that the acid, $C_7H_{13}\cdot COOH$, which melts at 245—248° and yields an amide melting at 195°, and was described as 1 : 4-ethylcyclopentanecarboxylic acid by Einhorn and Willstätter, is identical with Spiegel's cycloheptanecarboxylic acid.

The three ethylcyclopentenecarboxylic acids are in reality cyclo-heptenecarboxylic acids, the one melting at 50° being identical with Spiegel's suberenecarboxylic acid.

Hydrotropilidinecarboxylic acid is a cycloheptadienecarboxylic acid in which the position of the ethylene linkings is unknown.

Finally, the three paramethylenedihydrobenzoic acids or tropilidine-carboxylic acids are cycloheptatrienecarboxylic acids, whilst Buchner's a-isophenylacetic acid (Abstr., 1898, i, 639) is the fourth possible isomeride.

These facts, moreover, render it extremely probable that tropilidine itself is cycloheptatriene, whilst hydrotropilidine is cycloheptadiene.

<div align="right">A. H.</div>

Interchange of Halogens in the Aromatic Series. By VICTOR THOMAS (*Compt. rend.*, 1898, **127**, 184—186).—When 1 : 4-dibromo-benzene is heated in a reflux apparatus with from ten to twelve times its weight of anhydrous ferric chloride, there is abundant evolution of hydrogen chloride, and the principal product of the reaction is penta-chlorobromobenzene, C_6Cl_5Br, which crystallises in long needles melting at 228°. In this reaction, the ferric chloride effects the displacement of 1 atom of bromine in the dibromobenzene by chlorine, an inter-change which is common in the aliphatic, but rare in the aromatic, series. The bromine is not evolved as hydrogen bromide, but enters into combination with the iron to form a bromide or, perhaps, a chlorobromide. Whether the displacement of bromine by chlorine follows or precedes the further chlorination of the dibromobenzene, is a problem which the author hopes to solve by a study of the bye-products of the reaction. These are formed in very small quantity, and consist of a white substance melting at about 20°, and a compound crystallising in needles, melting at 120°, and readily subliming. N. L.

Pyrogenic Decomposition of Gas-oil, Phenol, and Cresol. By E. MÜLLER (*J. pr. Chem.*, 1898, **58**, [ii], 1—50).—The substance to be decomposed was allowed to flow into an iron tube, 120 cm. long by 1·3 cm. wide, placed in a combustion furnace and tilted slightly downwards; a length of 65 cm. was heated in the furnace by means of direct flames, the last half to 700—800°, the first half to a rather lower temperature; the ends of the tube surrounding the india-rubber bungs were jacketed with a current of cold water. The products of decomposition were passed first through a distillation flask of 150 c.c. capacity kept cool with ice and salt, and then through a tower, 5 cm. wide by 30 cm. high, fitted with 24 horizontal plates, each bored with a few holes in such a way that the holes in one plate were never directly above those in the plate below : the tar condensed in the flask, and in the tower smoky matter was deposited. After leaving the tower, the gas, now colourless, passed a Winkler's spiral washing apparatus and two wash bottles, all filled with petroleum; after this, it was collected in the gasometer, which consisted of two large glass carboys of some 60 L. capacity containing water. In some cases, three wash bottles containing ammoniacal silver nitrate and then two containing sulphuric acid were inserted between the tower and the petroleum absorption vessels; in them, the acetylene was absorbed, and it was estimated by filtering off the impure silver acetylide, decomposing it with hydrochloric acid, dissolving out the silver chloride with ammonia, reprecipitating and weighing it; the amount of acetylene was always very small. The benzene formed was determined by distilling the tar and contents of the petroleum absorption vessels, collecting what came over below 120°, nitrating this, distilling the nitrobenzene over with steam, extracting it from the distillate with ether, and weighing; more benzene condensed in the tar than passed on with the gas. By dissolving the residual tar in chloroform and precipitating with light petroleum, the solid hydrocarbons, including naphthalene, could be isolated. The density of the moist gas obtained was compared with that of moist air by observing the rates of flow of the two gases through a capillary orifice; the density of the gas when dry was then calculated. Finally, a residue of solid carbon was left in the iron tube.

The table on page 28 gives the results of the experiments.

The experiment with gas oil was made for purposes of comparison; the gas contained much ethylene and had a good illuminating power, and practically no carbon was left in the tube. With phenol, the volume of gas obtained was nearly as great, but it contained little ethylene and had practically no illuminating power, and there was a large amount of soot formed; from the composition of the gas, it would seem that the bulk of the phenol decomposes according to the equation $C_6H_6O = CO + 3H_2 + 5C$. With cresol, the results were similar, except that more methane and benzene were produced, and the gas had a feeble illuminating power; the decomposition appears to take place largely according to the equation $CH_3 \cdot C_6H_4 \cdot OH = CO + CH_4 + 2H_2 + 5C$. In two experiments, when the cresol was fed in rather more quickly, and as a consequence the temperature in the iron tube somewhat reduced, a very large quantity of tar was obtained with a smaller quantity of gas, and but little coke remained in the tube. With

Quantities are given per 100 grams of material used.	Gas oil.	Phenol.	Cresol.	Gas oil and phenol.	Gas oil and cresol.	Oil of turpentine b. p. 155—160°.
Material used ⎰ per ⎱ grams.	0·5	0·44	0·20	0·34	0·52	0·23
Gas evolved ⎰ minute, ⎱ c.c.	240	282	132	132	240	126
Gas obtained (at 0° and 760 mm.) litres.	44·68	64·81	60·30	39·75	46·00	60·01
1 litre of dry gas weighed. grams	1·012	0·562	0·600	0·736	0·815	0·629
Composition of gas :—						
Ethylene............... grams	27·6	1·05	1·1	9·7	10·8	6·7
Carbonic oxide...... ,,	0·9	24·9	21·9	7·3	9·6	2·5
Hydrogen............. ,,	0·3	3·4	2·7	1·2	1·0	1·7
Methane .... ,,	15·2	4·1	8·2	9·6	12·9	23·8
Distillate below 120°:						
Weight .... grams	12·8	7·8	16·6	8·0	17·0	15·0
Sp. gr.............................	0·801	0·910	0·899	0·910	0·903	0·888
Benzene................. grams	5·8	4·4	10·5	5·2	8·5	6·0
Percentage yield :—						
Gas	44	33·5	34	27·5	34	34·5
Carbon	—	29	28	2	0·5	1·5
Tar and petroleum absorption	51·5	28	32	64	59	52
Loss.............................	4·5	9·5	6	6·5	6·5	12

mixtures of gas oil with either phenol or cresol in equal proportions, both parts of the mixture undergo decomposition, and the gas, as regards composition and illuminating power, stands between those obtained with the pure constituents ; there is practically no formation of coke, however. If the temperature is reduced a little below 700°, by feeding in the material faster, only the gas oil undergoes decomposition ; the phenol distils over unchanged and is collected with the tar. With oil of turpentine, which contains several methyl groups, the amount of methane present in the gas is very large.

<div align="right">C. F. B.</div>

Constitution of the Nitramidophenol which is produced by the action of Sulphuric Acid on Orthonitrodiazobenzenimide. By FRIEDRICH KEHRMANN and ERNST GAUHE (*Ber.*, 1898, **31**, 2403—2405. Compare Abstr., 1898, i, 45, and this vol., i, 31). —The nitramidophenol prepared from orthonitrodiazobenzenimide by the action of sulphuric acid is converted by reduction into *4-hydroxyorthophenylenediamine*, $C_6H_3(NH_2)_2 \cdot OH$, the *hydrochloride* of which crystallises in thick, almost colourless tablets. The *triacetyl* derivative of this base crystallises in colourless needles, melts at 184—185°, and is converted by dilute aqueous soda into *diacetamidophenol*, $OH \cdot C_6H_3 \cdot (NHAc)_2$, which crystallises in prisms melting at 205—207°. This substance is converted by oxidation into acetamidoquinone, the formation of which proves the constitution of the foregoing compounds.

<div align="right">A. H.</div>

General Method for the Preparation of Mixed Carbonates of the Fatty and Aromatic Series. By PAUL CAZENEUVE and ALBERT MOREL (*Compt. rend.*, 1898, **126**, 1871—1873).—Mixed carbonates of the fatty and aromatic series are readily obtained by heating normal phenylic carbonate or its homologues with the alcohols of the fatty series in presence of certain organic bases, such as carbamide. In this way, phenylic alkylic carbonates have been prepared containing methyl, ethyl, propyl, isopropyl, isobutyl, isoamyl, and allyl. With the alcohols of higher molecular weight, some allophanates and urethanes are formed, but these secondary products can be avoided by using aniline, dimethylaniline, pyridine, quinoline, and some other bases in place of carbamide. Mixed alkylic carbonates of guaiacol, thymol, and tolyl were prepared in the same way.

In the absence of a base, little or no reaction takes place. Most probably the bases first form alcoholates which afterwards react in this manner, $CO(OPh)_2 + C_5NH_5,EtOH = OEt\cdot CO\cdot OPh + C_5NH_5,PhOH$.

When sodium ethoxide, dissolved in alcohol, is added to a well cooled solution of phenylic carbonate in ether–alcohol, phenylic ethylic carbonate is obtained in considerable quantity. In several cases, this reaction affords a better method of preparing the mixed carbonates than the other reaction just described. C. H. B.

Mixed Phenylic Alkylic Carbonates. By PAUL CAZENEUVE and ALBERT MOREL (*Compt. rend.*, 1898, **127**, 111—113).—The following mixed ethereal carbonates have been prepared by the general method indicated by the authors in a previous communication (compare preceding abstract).

Phenylic methylic carbonate, obtained by heating phenylic carbonate and carbamide in excess of methylic alcohol, boils at 190—200° under a pressure of 754 mm., and at 123° under 44 mm. ; its sp. gr. = 1·1607 at 0°.

Phenylic propylic carbonate boils at 210—220° (750 mm.), and at 120—130° (30 mm.) ; its sp. gr. = 1·0756 at 0°.

Phenylic isopropylic carbonate boils at 220° (750 mm.), and at 141—142° (70 mm.).

Phenylic isobutylic carbonate, obtained by heating phenylic carbonate and isobutylic alcohol with pyridine, boils at 220—225° (750 mm.), and at 130° (30 mm.) ; its sp. gr. = 0·9941 at 0°.

Phenylic isoamylic carbonate, produced like the preceding compound, boils at 220° (760 mm.), and at 120—130° (60 mm.) ; its sp. gr. = 1·0 at 0°.

These mixed carbonates are all colourless liquids with an agreeable odour and are miscible with the usual organic solvents.

Phenylic allylic carbonate, which is a colourless liquid with an alliaceous odour, boils at 130° under a pressure of 70 mm. G. T. M.

Action of Bromine on 1 : 4-Tertiary Butylphenol in Presence of Aluminium Bromine. By F. BODROUX (*Compt. rend.*, 1898, **127**, 186—188).—1 : 4-Tertiary butylphenol, $CMe_3\cdot C_6H_4\cdot OH$, reacts vigorously with bromine in the presence of aluminium bromide, with the formation of a substance which analysis shows to be pentabromophenol. As a general rule, when monhydric phenols are treated

with bromine in the presence of aluminium bromide, the maximum substitution occurs in the benzene nucleus. A side chain attached to the nucleus through a C or CH group is destroyed, and an atom of bromine takes its place. If, on the other hand, the linking is effected by a CH_2 group, the side chain remains unaffected. N. L.

Nitration and Oxidation Products of Phenols which are Insoluble in Alkalis. By KARL AUWERS and F. RAPP (*Annalen*, 1898, **302**, 153—171. Compare Auwers, Abstr., 1897, i, 336).—The *compound*, $C_8H_6Br_3NO_3$, obtained by the action of fuming nitric acid on tribromortho-xylenol, separates from petroleum in small, lustrous crystals, and melts at 97—99°; the *compound* from tribromopara-xylenol melts at 85—86°. The *compound*, $C_9H_9Br_2NO_3$, from dibromomesitol, forms hexagonal crystals, and melts at 72°.

The *compound*, $C_8H_7Br_3O_2$, produced on heating a glacial acetic acid solution of the nitro-compound from tribromortho-xylenol, crystallises in long prisms, and melts at 178—180°; dibromopara-xyloquinone is formed when the nitro-compound from tribromopara-xylenol is treated in the same way, whilst the nitro-compound from dibromomesitol yields the *compound*, $C_9H_{10}Br_2O_2$, which crystallises from petroleum in lustrous prisms, and melts at 132°.

It has been pointed out (*loc. cit.*) that, when heated in glacial acetic acid, the nitro-compound from dibromo-ψ-cumenol yields the compound $C_9H_{10}Br_2O_2$, which is identical with the substance obtained by Zincke from dibromo-ψ-cumenol under the influence of dilute nitric acid (Abstr., 1896, i, 214); the *acetyl* and *diacetyl* derivatives melt at 95—96° and 102—103° respectively. Hydrogen chloride is without action on the substance, but in presence of zinc chloride converts it into the chloride of dibromanhydroparahydroxy-ψ-cumylic alcohol which melts at 110°; the same compound is produced by the action of phosphorus pentachloride, whilst hydrogen bromide and phosphorus pentabromide give rise to dibromo-ψ-cumenol.

The constitution of the nitro-compounds is discussed in the original paper. M. O. F.

Ethanedicathechol [Dicatechol Acetylenic Ether]. By CHARLES MOUREU (*Compt. rend.*, 1898, **127**, 69—71. Compare Abstr., 1898, 644).—Acetylene dibromide interacts violently with a solution of catechol in aqueous or alcoholic potash; spontaneously inflammable monobromacetylene is evolved, whilst catechol acetylenic ether, the normal and expected product of the reaction, appears not to be formed. With acetylene tetrabromide, on the contrary, a definite condensation product is formed, which may be separated by steam distillation from the other products of the reaction; this compound crystallises from alcohol in thin leaves melting at 88—89°, and is shown by analysis, and by a cryoscopic determination of its molecular weight (found, 235; theory, 242) to have the formula $C_{14}H_{10}O_4$, corresponding with *dicatechol acetylenic ether*,

$$C_6H_4 {<}^O_O{>} CH \cdot CH {<}^O_O{>} C_6H_4.$$
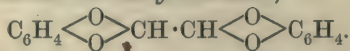
On hydrolysis with dilute sulphuric acid, it yields catechol and a *substance* which, after purification, crystallises in white, nacreous leaves

melting at 130—131°, and is shown by analysis, and by an ebullioscopic molecular weight determination (found, 160; theory, 168) to have the formula $C_8H_8O_4$. This compound, the constitution of which will be discussed hereafter, is slightly soluble in cold water, and readily in hot water, alkalis, and organic solvents; the aqueous solution reduces an ammoniacal solution of silver nitrate, and gives an intense blue coloration with ferric chloride. N. L.

Amidoquinone. By FRIEDRICH KEHRMANN and GABRIEL BAHATRIAN (*Ber.*, 1898, **31**, 2399—2403).—*Triacetyldiamidophenol*,

$$OAc \cdot C_6H_3(NHAc)_2,$$
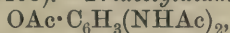
obtained by the action of acetic anhydride and sodium acetate on diamidophenol, crystallises in colourless needles and melts at 180—182°. When it is dissolved in dilute aqueous soda and the solution acidified, the precipitate consists of *diacetamidophenol*, $OH \cdot C_6H_3(NHAc)_2$, which crystallises in colourless needles melting at 220—222°, and is converted by oxidation with sodium dichromate and sulphuric acid into *acetamidoquinone*, $C_6H_3O_2 \cdot NHAc$; the latter crystallises in reddish-yellow, thick prisms melting at 142°. It has been found impossible to convert this compound into amidoquinone. *Acetamidoquinol*, $NHAc \cdot C_6H_3(OH)_2$, obtained by reducing the foregoing compound with sulphurous acid, forms greyish-white, granular crystals melting at 100°. *Anilidoacetamidoquinone*,

$$NHPh \cdot C_6H_2O_2 \cdot NHAc,$$
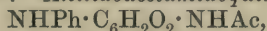
obtained on adding aniline to an alcoholic solution of acetamidoquinone, crystallises in almost black, glistening needles which melt and decompose at 278—280°. *Phenyldiamidoquinone*,

$$NHPh \cdot C_6H_2O_2 \cdot NH_2,$$
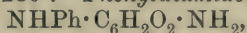
obtained by the reduction of the anilido-compound with stannous chloride and hydrochloric acid, crystallises in violet-brown plates melting at 280—282°. When it is heated with dilute aqueous soda, it is converted into 1 : 4-dihydroxyquinone and *anilidohydroxyquinone*, $NHPh \cdot C_6H_2O_2 \cdot OH$; the latter crystallises in plates having a violet surface-lustre, and melting and decomposing at 228—230°. The formation of 1 : 4-dihydroxyquinone by the action of alkalis on this compound and on phenyldiamidoquinone, proves the constitution of anilidoacetamidoquinone. When acetamidoquinone is treated with concentrated hydrochloric acid, it is converted into *chloracetamidoquinol*, and this, on oxidation with chromic acid, passes into *chloracetamidoquinone*, $C_6H_2ClO_2 \cdot NHAc$; the latter crystallises in golden-yellow prisms melting at 174—175°, and is converted by aniline into anilidoacetamidoquinone. The corresponding bromine *compound* crystallises in large, golden-yellow plates melting at 183—185°. A. H.

Condensation Products of Phloroglucinol and of Phloroglucide. By JOSEF HERZIG (*Monatsh.*, 1898, **19**, 376—383).—When triacetylphloroglucinol is hydrolysed with sulphuric acid, in order to determine the number of acetyl groups present, a yellow condensation product is obtained when the acid is of a certain strength. If the acetyl derivative is heated for an hour on the water bath with a mixture of equal volumes of sulphuric acid and water, the theoretical yield of acetic acid is obtained, and none of the yellow compound is

formed.   By the use of a stronger acid and of a higher temperature, less than the theoretical amount of acetic acid is obtained, namely, 5 molecules from 2 of the acetyl derivative, and the yellow condensation product is also formed.   The best results are obtained at a temperature of 130—140°, and with an acid containing 2 volumes of sulphuric acid to 1 of water.   These results indicate that 1 molecule of acetic acid is employed in condensing 2 molecules of phloroglucinol to the yellow compound.

Acetylphloroglucinol diethylic ether, $C_6H_3(OEt)_2 \cdot OAc$, crystallises from hot alcohol in long, colourless needles melting at 54—55°. When heated on the water bath with equal volumes of sulphuric acid and water, the theoretical amount of acetic acid is obtained (namely, 1 molecule), but when heated with two volumes of acid and one of water at 130—140°, only half the theoretical yield of acetic acid is obtained, and a yellow condensation product is also formed.   Similar results are given with acetylphloroglucinol monethylic ether.   These condensation products are probably to be regarded as anhydrides; when hydrolysed with alkalis, they yield, not phloroglucinol, but a substance which is probably phloroglucide.   With acetylphloroglucide, $C_{12}H_5(OAc)_5$, it is found that a condensation product is formed from 1 molecule of acetic acid and 1 of the phloroglucide.   J. J. S.

Homologous Phloroglucinols from Filicic Acid and from Aspidin. By RUDOLF BOEHM (*Annalen*, 1898, **302**, 171—191. Compare Weidel, Abstr., 1898, i, 578).—By heating filicic acid with zinc dust and 15 per cent. caustic soda on a water bath during 8 hours, phloroglucinol, methylphloroglucinol, dimethylphloroglucinol, and trimethylglucinol are produced; aspidin, when heated with caustic soda in a silver dish, yields filicic acid and the methyl ether of methylphloroglucinol.

Dibromomethylphloroglucinol, $C_7H_6Br_2O_3$, prepared by adding bromine to a solution of the phenol in glacial acetic acid, crystallises from dilute alcohol in elongated, thin prisms containing $3H_2O$, and melts indefinitely at 120—125°; it becomes anhydrous at 100°, and in this condition melts at 137° when slowly heated. *Tribenzoylmethylphloroglucinol* crystallises from alcohol in colourless prisms, and melts at 111—112°; *benzeneazomethylphloroglucinolazobenzene* forms beautiful, red needles, and melts at 236—237°.

*Tribromotrimethylphloroglucinol*, $C_9H_{11}Br_3O_3$, crystallises from alcohol in colourless, six-sided prisms and melts at 88—90°.   M. O. F.

Anhydroparahydroxymesitylic Alcohol and its Products of Change. By KARL AUWERS and H. ALLENDORFF (*Annalen*, 1898, **302**, 76—98.   Compare Abstr., 1898, i, 646).—The *bromide* of dibromanhydroparahydroxymesitylic alcohol, $CBr\Big\langle {{CBr:CMe} \atop {CBr:CMe}} {{} \atop {CH_2——O}} \Big\rangle CH$, prepared by the action of bromine dissolved in glacial acetic acid on mesitol, crystallises in elongated, lustrous needles, and melts at 146—147°; phenylic cyanate in benzene at 100° converts it into the *compound* $C_{16}H_{14}Br_3NO_2$, which melts at 226°.

*Dibromoparahydroxymesitylic ethylic ether*,

$$OEt \cdot CH_2 \cdot C \lessgtr^{CBr \cdot CMe}_{CBr:CMe} > C \cdot OH,$$
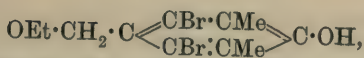
obtained on treating the bromide with boiling absolute alcohol, crystallises from petroleum in lustrous, white prisms, and melts at 147°. The *acetyl* derivative separates in lustrous needles, and melts at 88°.

Dibromoparahydroxymesitylaniline,

$$NHPh \cdot CH_2 \cdot C \lessgtr^{CBr \cdot CMe}_{CBr:CMe} > C \cdot OH,$$
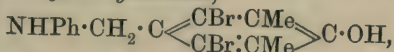
produced by the action of aniline, dissolved in benzene, on the bromide, crystallises from alcohol in yellowish, flattened prisms, and melts at 136—137°; the *phenylurethane* separates from benzene in white needles, and melts at 183°. *Dibromoparahydroxymesitylpiperidine,* prepared in a similar manner from piperidine, crystallises from alcohol in prisms melting at 134°; the *acetyl* derivative forms lustrous, white needles, and melts at 122—123°.

The *acetate* of dibromanhydroparahydroxymesitylic alcohol,

$$OAc \cdot C \lessgtr^{CBr:CMe}_{CH_2 \overline{\quad} O} \gtrdot CH,$$
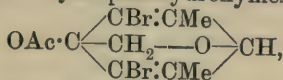
obtained by adding sodium acetate (1 mol.) to a solution of the bromide in hot acetic acid, crystallises from benzene in small, lustrous prisms, and melts at 165—166°. Cold caustic soda converts it into 2 : 6 : 2′ : 6′-*tetrabromo*-3 : 5 : 3′ : 5′-*tetramethylparadihydroxystilbene*,

$$C_2H_2(C_6Br_2Me_2 \cdot OH)_2,$$
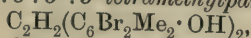
which crystallises from benzene in small needles, and melts at 232° when heated rapidly; the *diacetyl* derivative forms white needles and melts at 244°.
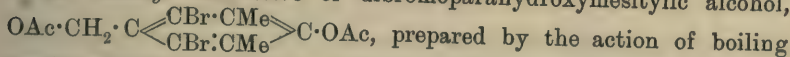
The *diacetyl* derivative of dibromoparahydroxymesitylic alcohol, $OAc \cdot CH_2 \cdot C \lessgtr^{CBr \cdot CMe}_{CBr:CMe} > C \cdot OAc$, prepared by the action of boiling acetic anhydride on the acetate of dibromanhydroparahydroxymesitylic alcohol during 2 hours, crystallises in lustrous, white needles, and melts at 159—160°; hydrogen bromide acting on the substance dissolved in glacial acetic acid regenerates the bromide (m. p. 146—147°).
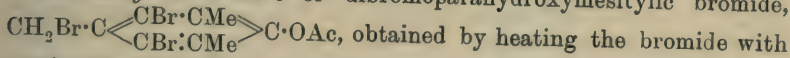
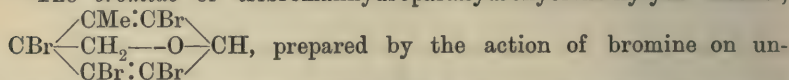The *acetyl* derivative of dibromoparahydroxymesitylic bromide, $CH_2Br \cdot C \lessgtr^{CBr \cdot CMe}_{CBr:CMe} > C \cdot OAc$, obtained by heating the bromide with acetic anhydride during several hours, crystallises in beautiful, long needles, several centimetres in length, and melts at 150—151°. Alcoholic potash converts it into dibromoparahydroxymesitylic ethylic ether, which is also produced by the action of alcohol in sealed tubes at 100°; silver oxide gives rise to the *diacetyl* derivative of tetrabromoparadihydroxydimesitylic ether, $O(CH_2 \cdot C_6Br_2Me_2 \cdot OAc)_2$, which crystallises in white needles and melts at 228—229°. The *compound*, $C_{22}H_{20}Br_4O_4$, is obtained by the action of alcoholic sodium ethoxide (1 mol.) on the acetyl derivative of dibromoparahydroxymesitylic bromide; it melts at 217—218°. The *isobutyryl* derivative of dibromoparahydroxymesitylic bromide crystallises from alcohol in lustrous needles and melts at 152—154°.

Dibromoparahydroxymesitylic alcohol, $OH \cdot CH_2 \cdot C \lessgtr^{CBr \cdot CMe}_{CBr:CMe} > C \cdot OH,$

is obtained by heating the bromide of dibromanhydroparahydroxy-mesitylic alcohol with aqueous acetone in a reflux apparatus, the crystalline product being extracted with glacial acetic acid, in which a less readily fusible bye-product remains undissolved; it melts at 191—192° when heated rapidly, but if the temperature rises slowly, the substance forms a turbid liquid at 188°, subsequently solidifies, and finally melts at 240—250°. This is due to its conversion into an isomeric *compound* which melts at 252°, and is transformed into the alcohol when the solution in benzene or xylene is boiled. Hot acetic anhydride converts the alcohol into the acetyl derivative of dibromanhydropara-hydroxymesitylic alcohol.　　　　　　　　　　　　　　　M. O. F.

Derivatives of Anhydroparahydroxyortho-xylylic Alcohol, and of Anhydro-orthohydroxypseudocumylic Alcohol. By KARL AUWERS and H. VAN DE ROVAART (*Annalen*, 1898, **302**, 99—107).—The *bromide* of tribromanhydroparahydroxyortho-xylylic alcohol,

$$CBr{<}{\overset{CMe\colon CBr}{\underset{CBr\colon CBr}{CH_2{-}{-}O}}}{>}CH,$$ prepared by the action of bromine on un-

symmetrical ortho-xylenol, crystallises from boiling glacial acetic acid in lustrous needles, and melts at 171—173°.

Tribromoparahydroxyortho-xylylic methylic ether,

$$OMe\cdot CH_2\cdot C{<}{\overset{CMe\cdot CBr}{\underset{CBr\colon CBr}{}}}{>}C\cdot OH,$$
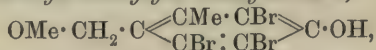
formed when the bromide is treated with boiling methylic alcohol, crystallises from petroleum in silky needles, and melts at 122—123°.

Tribromoparahydroxyortho-xylylaniline,

$$NHPh\cdot CH_2\cdot C{<}{\overset{CMe\cdot CBr}{\underset{CBr\colon CBr}{}}}{>}C\cdot OH,$$
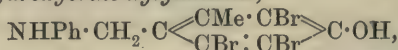
produced on adding a solution of aniline (2 mols.) in benzene to the bromide, melts somewhat indefinitely at 120—125°. *Tribromopara-hydroxyortho-xylylpiperidine*, crystallises in reddish needles, and melts at 155—158°.

The *acetyl* derivative of tribromanhydroparahydroxyortho-xylylic alcohol, $OAc\cdot C{<}{\overset{CMe\colon CBr}{\underset{CBr\colon CBr}{CH_2{-}{-}O}}}{>}CH$, obtained on adding sodium acetate

(1 mol.) to a solution of the bromide in hot acetic acid, crystallises from benzene in small, white needles, and melts at 142—143°.

The *acetyl* derivative of tribromoparahydroxyortho-xylylic bromide, $CH_2Br\cdot C{<}{\overset{CMe\cdot CBr}{\underset{CBr\colon CBr}{}}}{>}C\cdot OH$, is formed by the action of acetic anhy-

dride on the bromide of tribromanhydroparahydroxyortho-xylylic alcohol, and crystallises from glacial acetic acid in small, lustrous needles; it melts at 138—140°, and is indifferent towards hot, aqueous alkalis.

Orthohydroxy-ψ-cumylic alcohol, $OH\cdot C_6H_2Me_2\cdot CH_2\cdot OH$, is prepared by treating a solution of ortho-xylenol in caustic soda with aqueous formaldehyde; after an interval of 2 days, the liquid is nearly neutralised with acetic acid, and saturated with carbonic anhydride, which precipitates the hydroxy-alcohol. It crystallises from

xylene in nacreous leaflets and needles melting indefinitely at 108—114°.

The *bromide* of bromanhydro-orthohydroxy-ψ-cumylic alcohol,

$$C_6H_2Me_2Br_2 {<}^{CH_2}_{O},$$
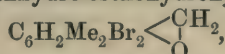
formed on adding bromine in glacial acetic acid to a solution of the hydroxy-alcohol in the same medium, crystallises from light petroleum in needles, and melts at 66—67°.　　　　　　　　　　M. O. F.

Parahydroxypseudocumylic Alcohol and its Products of Bromination. By KARL AUWERS and H. ERCKLENTZ (*Annalen*, 1898, **302**, 107—130. Compare Auwers and Baum, Abstr., 1897, i, 34).— *Dibromopara-xylenol*, [Me$_2$: Br$_2$: OH = 1 : 4 : 2 : 5 : 6], is prepared by adding bromine (2 mols.) dissolved in glacial acetic acid to para-xylenol in the same medium, from which it crystallises in large, lustrous needles melting at 79°. The bromo- and tribromo-derivatives, which melt at 87° and 177—178° respectively, have been described by Jacobsen ; the *benzoyl* derivative of tribromopara-xylenol crystallises in small, white needles, and melts at 89—90°.

Parahydroxy-ψ-cumylic alcohol, $OH \cdot C_6H_2Me_2 \cdot CH_2 \cdot OH$, prepared from para-xylenol and formaldehyde (compare foregoing abstract), crystallises from ethylic acetate in lustrous, rhombic plates, melts at about 165°, and loses water at 160°. The *methylic ether*,
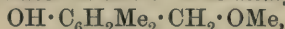
$$OH \cdot C_6H_2Me_2 \cdot CH_2 \cdot OMe,$$

obtained on heating the substance with methylic alcohol at 150—160°, forms aggregates of lustrous needles, and melts at 101°. The *dimethylic ether*, $OMe \cdot C_6H_2Me_2 \cdot CH_2 \cdot OMe$, results from the action of methylic iodide and sodium methoxide ; it melts at 88°, and boils at 129° under a pressure of 16·5 mm.

The *bromide* of bromanhydroparahydroxy-ψ-cumylic alcohol,

$$CBr {<}^{CMe:CBr}_{CH:CMe} {>} CH,$$
$$CH_2——O$$
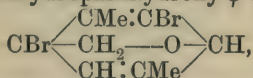
obtained on adding a solution of bromine in chloroform to para-hydroxy-ψ-cumylic alcohol suspended in the same medium, crystallises from glacial acetic acid in long, lustrous needles, and melts at 81°. Bromine acts vigorously on the substance, converting it into the bromide of dibromanhydroparahydroxy-ψ-cumylic alcohol ; zinc and hydrochloric acid reduce it to bromo-ψ-cumenol, which melts at 32°.

Bromoparahydroxy-ψ-cumylaniline,

$$NHPh \cdot CH_2 \cdot C {<}^{CMe \cdot CBr}_{CH{=}CMe} {>} C \cdot OH,$$
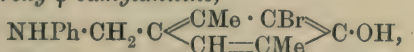
formed by the action of aniline on the bromide, crystallises from petroleum in leaflets, and melts at 75°. *Bromoparahydroxy-ψ-cumyl piperidine* crystallises from alcohol in small needles, and melts at 81—82°.

Bromoparahydroxy-ψ-cumylic ether, $O(CH_2 \cdot C_6HMe_2Br \cdot OH)_2$, prepared by boiling the bromide with aqueous acetone, after crystallisation from boiling benzene, melts at 162° ; concentrated sulphuric acid develops a carmine-red coloration. The *diacetyl* derivative separates

d 2

from glacial acetic acid in slender, lustrous needles, and melts at 140°. The *thio-ether*, $S \cdot C_2H_4(C_6HMe_2Br \cdot OH)_2$, obtained on agitating the bromide with aqueous potassium sulphide, melts at 152°.

The *acetyl* derivative of bromanhydroparahydroxy-ψ-cumylic alcohol,

$$OAc \cdot C \underset{CH=CMe}{\overset{CMe \,\vdots\, CBr}{\diagdown \diagup}} CH,$$

formed on adding sodium acetate (1 mol.) to a boiling solution of the bromide in glacial acetic acid, crystallises in lustrous needles and melts at 65°. The *chloride*, $C_9H_{10}BrClO$, is obtained on passing hydrogen chloride into a solution of the acetyl derivative in methylic alcohol, and melts at 73—74°; the *iodide* melts at 94°.

The *diacetyl* derivative of bromoparahydroxy-ψ-cumylic alcohol,

$$OAc \cdot CH_2 \cdot C \underset{CH=CMe}{\overset{CMe \cdot CBr}{\diagdown \diagup}} C \cdot OAc,$$

prepared by treating the foregoing acetyl derivative with boiling acetic anhydride, crystallises from light petroleum in flattened prisms, and melts at 83—84°.

Bromoparahydroxy-ψ-cumylic alcohol,

$$OH \cdot CH_2 \cdot C \underset{CH=CMe}{\overset{CMe \cdot CBr}{\diagdown \diagup}} C \cdot OH,$$

obtained on hydrolysing the diacetyl derivative with alcoholic potash, crystallises from petroleum in lustrous needles, and melts at 90—91°. Acetic chloride converts it into the acetyl derivative of bromanhydroparahydroxy-ψ-cumylic alcohol (m. p. 65°).

The *acetyl* derivative of bromoparahydroxy-ψ-cumylic bromide,

$$CH_2Br \cdot C \underset{CH=CMe}{\overset{CMe \cdot CBr}{\diagdown \diagup}} C \cdot OAc,$$

prepared by the action of boiling acetic anhydride on the bromide of bromanhydroparahydroxy-ψ-cumylic alcohol (m. p. 81°), crystallises from petroleum in small, silky needles and melts at 92—93°. The *acetyl isobutyryl* derivative of bromoparahydroxy-ψ-cumylic alcohol, $C_4H_7O \cdot O \cdot CH_2 \cdot C \underset{CH=CMe}{\overset{CMe \cdot CBr}{\diagdown \diagup}} C \cdot OAc$, obtained from the foregoing substance and silver isobutyrate, separates from its solution in light petroleum in lustrous, transparent prisms, and melts at 49—50°.

The *isobutyryl* derivative of bromoparahydroxy-ψ-cumylic bromide,

$$CH_2Br \cdot C \underset{CH=CMe}{\overset{CMe \cdot CBr}{\diagdown \diagup}} C \cdot O \cdot C_4H_7O,$$

crystallises from petroleum in lustrous needles, and melts at 91°; the *acetyl* derivative,

$$OAc \cdot CH_2 \cdot C \underset{CH=CMe}{\overset{CMe \cdot CBr}{\diagdown \diagup}} C \cdot O \cdot C_4H_7O,$$
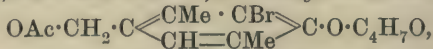
obtained from it by the action of silver acetate, crystallises from well cooled solutions in light petroleum, and melts at 39—40°.

M. O. F.

Bromination Products of Saligenin. By KARL AUWERS and G. BÜTTNER (*Annalen*, 1898, **302**, 131—152).—According to the experimental conditions, the bromination of saligenin proceeds in three different directions. Treatment in aqueous solution with bromine water at the ordinary temperature gives rise to bromosaligenin and dibromosaligenin; at 50—60°, the same agent produces tribromo-

phenol, bromanil, and Benedikt's ketobromide, which probably has the constitution, $CBr{<}^{CH \cdot CBr_2}_{CH : CBr}{>}CO$ (Abstr., 1880, 246); finally, bromination in organic solvents yields the bromides of bromanhydrosaligenin and of dibromanhydrosaligenin. These bromides resemble those of the parahydroxy-alcohols and paramethylphenols in their behaviour towards alcohols, bases, water, organic anhydrides, and sodium acetate in presence of acetic anhydride; they are indifferent, however, to alkali sulphides, and yield compounds with sodium acetate in acetic acid which differ from those derived from the bromides hitherto described. Moreover, unlike the latter, the acetyl derivatives corresponding with them, and the piperidine derivatives, are not converted into derivatives of stilbene.

Bromosaligenin, $OH \cdot C_6H_3Br \cdot CH_2 \cdot OH$ [$CH_2 \cdot OH : Br : OH = 1 : 2 : 5$], crystallises from benzene in large, lustrous leaflets, and melts at 107—$109°$; unlike saligenin, it does not develop a red coloration with concentrated sulphuric acid, but ferric chloride produces a blue coloration in the aqueous solution.

Dibromosaligenin [$CH_2 \cdot OH : OH : Br_2 = 1 : 2 : 3 : 5$] crystallises in long, white needles from a mixture of petroleum and benzene, and melts at 88—$89°$; ferric chloride develops a violet-blue coloration in the aqueous solution, but concentrated sulphuric acid is without action on the substance.

The *bromide* of bromanhydrosaligenin, $C_6H_4Br_2{<}^{CH_2}_{O}$, crystallises from benzene or petroleum in beautiful needles, and melts at $98°$; reduction with zinc and hydrochloric acid converts it into bromorthocresol, the action of aqueous acetone giving rise to bromosaligenin. *Bromorthocresylaniline*, $OH \cdot C_6H_3Br \cdot CH_2 \cdot NHPh$, formed on adding a benzene solution of aniline to the bromide, crystallises from dilute alcohol in rhombohedra, and melts at 114—$115°$. *Bromorthocresylpiperidine* melts at 63—$64°$.

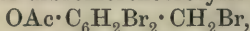The *acetyl* derivative of bromorthocresylic bromide,
$$OAc \cdot C_6H_3Br \cdot CH_2Br,$$
formed by the action of boiling acetic anhydride on the bromide of bromosaligenin, crystallises from alcohol in long, white needles, and melts at 63—$64°$. The *acetyl* derivative of bromosaligenin is produced if sodium acetate is present, and crystallises from petroleum in long, silky needles melting at 100—$101°$.

The *bromide* of dibromanhydrosaligenin, $C_6H_3Br_3{<}^{CH_2}_{O}$, crystallises from glacial acetic acid in large, lustrous needles, and melts at 116—$118°$; reduction converts it into $3 : 5$-dibromorthocresol, and dibromosaligenin is obtained from it under the influence of boiling aqueous acetone.

Dibromorthocresylic methylic ether, $OH \cdot C_6H_2Br_2 \cdot CH_2 \cdot OMe$, prepared from the bromide by the action of boiling methylic alcohol, forms a pale yellow oil. *Dibromorthocresylaniline*, $OH \cdot C_6H_2Br_2 \cdot CH_2 \cdot NHPh$, crystallises from alcohol in needles, and melts at 98—$99°$, and *dibromorthocresylpiperidine* melts at 99—$100°$.

The *acetyl* derivative of dibromorthocresylic bromide,

$$OAc \cdot C_6H_2Br_2 \cdot CH_2Br,$$

separates from alcohol in white needles, and melts at 120—121°; silver acetate converts it into the diacetyl derivative of dibromo-saligenin, and piperidine gives rise to dibromorthocresylpiperidine. The *acetyl* derivative of dibromosaligenin, $OH \cdot C_6H_2Br_2 \cdot CH_2 \cdot OAc$, separates from alcohol in flattened, lustrous crystals, and melts at 110—112°; the *diacetyl* derivative crystallises in needles, and melts at 70—71°.   M. O. F.

Preparation of Cholesterol and Phytosterol from Animal and Plant Fats. By A. JUCKENACK and ALBERT HILGER (*Arch. Pharm.*, 1898, **236**, 367—369).—A reply to von Raumer (*Zeit. angw. Chem.*, 1898). The authors give the details of their method for the extraction of cholesterol and phytosterol from fats (compare *Forschungsber. Lebensmittel*, 1897, **119**, 128, 151) and add that, in the place of sea-sand, which is often impure, they now employ small pieces of moistened filter paper free from fat; the extraction with ether is by this means rendered much easier and more complete. It is also preferable to saponify with caustic soda instead of caustic potash, because the hard soap thus formed is easier to dry and pulverise. The ether used for extracting the soap should be dried over metallic sodium.   A. W. C.

Some Double Halogen Salts of Mercury. By J. N. SWAN (*Amer. Chem. J.*, 1898, **20**, 613—633).—*Aniline dimercurichloride*, $NH_2Ph,HCl,2HgCl_2$, is best prepared by dissolving the theoretical quantities of aniline hydrochloride and mercuric chloride in boiling water acidified with hydrochloric acid; on cooling, beautiful, white crystals separate, which dissolve sparingly in cold water, but much more readily in methylic and ethylic alcohol. Although no aniline salt containing a larger proportion of mercuric chloride than this can be obtained, on dissolving molecular proportions of aniline hydro-chloride and mercuric chloride in boiling water acidified with hydro-chloric acid, crystals of *aniline mercurichloride*, $NH_2Ph,HCl,HgCl_2$, separate; the latter appears to be decomposed to some extent when allowed to crystallise slowly from ethylic or methylic alcohol. *Dianiline mercurichloride*, $(NH_2Ph)_2,2HCl,HgCl_2$, prepared by adding an excess of aniline hydrochloride to a solution of mercuric chloride, crystallises in lustrous needles, and is much more soluble in water than either of the salts described above. No other compound of aniline with mercuric chloride could be obtained.

Orthotoluidine mercurichlorides.—(1), $C_7H_7NH_2,HCl,2HgCl_2$, prepared from carefully purified orthotoluidine, separates from very dilute hydro-chloric acid in beautiful, leaf-like crystals. (2), $C_7H_7 \cdot NH_2,HCl,HgCl_2$, prepared by carefully heating a solution of mercuric chloride with a slight excess of toluidine hydrochloride to the boiling temperature, closely resembles the corresponding aniline derivative. (3), $(C_7H_7 \cdot NH_2)_2,2HCl,HgCl_2$, crystallises in lustrous needles or prisms, is easily soluble in water, and is decomposed by boiling alcohol.

*Metatoluidine mercurichlorides.*—(1), $C_7H_7NH_2,HCl,2HgCl_2$, crystal-

lises in thin plates, and is somewhat less soluble in water than the corresponding orthotoluidine and aniline salts, although closely resembling them. (2), $C_7H_7 \cdot NH_2, HCl, HgCl_2$, and

$$(3), (C_7H_7 \cdot NH_2)_2, 2HCl, HgCl_2,$$
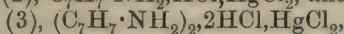
crystallise from very dilute hydrochloric acid in thin, lustrous plates.

Paratoluidine mercurichloride, $C_7H_7NH_2, HCl, HgCl_2$, is much more soluble in hot than in cold water, and crystallises in beautiful, long needles; it is the only mercury double salt that can be obtained from paratoluidine.

The formation of mixed halogen double salts of mercury and the amines seems to be possible; on dissolving orthotoluidine hydrochloride (4 grams) and mercuric bromide (12 grams) in 75 c.c. of water acidified with hydrochloric acid, and removing the mercuric bromide which first separates, lustrous needles of the *salt*,

$$C_7H_7NH_2, HCl, HgBr_2,$$
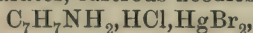
separate.

Although the salt, $MgCl_2, 3HgCl_2 + 5H_2O$, obtained by von Bonsdorff (*Ann. Phys. Chem.*, 1829, **17**, 115) from magnesium and mercuric chloride was prepared by the author, the salt, $MgCl_2, HgCl_2, 6H_2O$, described as separating from the mother liquor could not be obtained. The mercury strontium salt to which von Bonsdorff gave the formula $SrCl_2, 2HgCl_2 + 2H_2O$, is regarded as having the formula, $SrCl_2, 3HgCl_2 + xH_2O$, analogous to that of the magnesium salt. The barium salt, described as $BaCl_2, 2HgCl_2 + 2H_2O$, appears rather to be $BaCl_2, 3HgCl_2 + 8H_2O$.   W. A. D.

Double Halogen-salts of Tin with Aniline and the Toluidines. By ROBERT L. SLAGLE (*Amer. Chem. J.*, 1898, **20**, 633—646).— *Aniline stannochloride*, $NH_2Ph, HCl, SnCl_2 + H_2O$, prepared by boiling a solution of molecular quantities of aniline hydrochloride and stannous chloride in very dilute hydrochloric acid, crystallises in orthorhombic tables, $a:b:c := 0.4164 : 1 : 0.4608$; it is very soluble in hot water, sparingly in cold, and decomposes slowly in solution; in methylic and ethylic alcohol, it is extremely soluble. When heated, the salt commences to decompose at about 70°, and melts at about 110°; on heating more strongly, stannous chloride sublimes. When a solution of aniline stannochloride in dilute hydrochloric acid is left for several hours, crystals of the anhydrous stannichloride, $(NH_2Ph)_2, H_2SnCl_6$, are deposited. *Dianiline stannochloride*, $(NH_2Ph)_2, 2HCl, SnCl_2$, prepared by adding stannous chloride (1 mol.) to a solution of aniline hydrochloride (2 mols.), separates in monosymmetric crystals, and is much more soluble in water than the monaniline salt. No other compounds of aniline with stannous chloride could be obtained.

Dianiline stannichloride, $(NH_2Ph)_2, H_2SnCl_6 + 3H_2O$, prepared by dissolving molecular quantities of stannic chloride and aniline hydrochloride in dilute hydrochloric acid and boiling, separates in sheaf-like aggregates of needles which rapidly effloresce. Anhydrous, transparent crystals, however, can also be obtained which are perfectly stable; these have been measured by Hiortdahl (*Zeit. Kryst. Min.*, 1882, **6**, 484).

Orthotoluidine stannochloride, $C_7H_7\cdot NH_2,HCl,SnCl_2 + \frac{1}{2}H_2O$, the only salt obtainable from orthotoluidine and stannous chloride, separates in white, opaque prisms.   *Triorthotoluidine stannichloride*,

$$(C_7H_7NH_2)_3,3HCl,SnCl_4 + 2H_2O,$$

is formed on mixing solutions of orthotoluidine hydrochloride and stannic chloride in any proportion.

Metatoluidine stannochloride, $C_7H_7NH_2,HCl,SnCl_2 + \frac{1}{2}H_2O$, separates in silver-white, opaque crystals, and is the only stannous derivative obtainable from metatoluidine.   *Dimetatoluidine stannichloride*, $(C_7H_7NH_2)_2,H_2SnCl_6 + H_2O$, crystallises in monosymmetric tables, $a : b : c = 1\cdot924 : 1 : 1\cdot463 ; \beta = 86° \ 3'$.

Paratoluidine stannochloride, $C_7H_7NH_2,HCl,SnCl_2 + \frac{1}{2}H_2O$, closely resembles the corresponding aniline derivative, and is much less soluble in water than *diparatoluidine stannichloride*, $(C_7H_7NH_2)_2,H_2SnCl_6$. Diparatoluidine stannichloride has been described by Hiortdahl (*loc. cit.*).   W. A. D.

Double Halogen-salts of Zinc with Aniline and the Toluidines.

By Daniel Base (*Amer. Chem. J.*, 1898, **20**, 646—663).—Dianiline zincochloride, $(NH_2Ph)_2,H_2ZnCl_4 + H_2O$, formed on mixing zinc chloride with aqueous aniline hydrochloride, has been described by Vohl (*Dingl. poly. J.*, 1865, 211); if an excess of the hydrochloride (3—6 mols.) is employed, *trianiline zincochloride*, $(NH_2Ph)_3,3HCl,ZnCl_2 + 2H_2O$, separates in long, orthorhombic prisms; it is less soluble in alcohol and in water than the dianiline salt, and is stable in the air.   It loses the whole of its contained water when dried over sulphuric acid, and can be heated to 100° without decomposing.

Diorthotoluidine zincochloride, $(C_7H_7NH_2)_2,H_2ZnCl_4 + 2H_2O$ (Gräfinghoff, *J. pr. Chem.*, 1865, **95**, 221), is the only zinc double salt obtainable from orthotoluidine.

Dimetatoluidine zincochloride $(C_7H_7NH_2)_2,H_2ZnCl_4$, prepared by bringing together solutions of metatoluidine hydrochloride (1 mol.) and zinc chloride (2—3 mols.), separates from water, in which it is very soluble, in slender, silken needles.   When a larger proportion of metatoluidine hydrochloride is employed, *trimetatoluidine zincochloride*, $(C_7H_7NH_2)_3,3HCl,ZnCl_2$, is formed; it crystallises in slender needles, and is somewhat readily soluble in water.

Diparatoluidine zincochloride, $(C_7H_7NH_2)_2,H_2ZnCl_4$, formed on boiling a solution containing zinc chloride (1 mol.) and paratoluidine hydrochloride ($\frac{1}{3}$—3 mols.), crystallises in colourless plates, and dissolves easily in water.   *Triparatoluidine zincochloride*, $(C_7H_7NH_2)_3,3HCl,ZnCl_2$, formed in presence of an excess of paratoluidine hydrochloride, crystallises in well-defined, anorthic prisms.

Dianiline zincobromide, $(NH_2Ph)_2,H_2ZnBr_4 + H_2O$, the only double-salt obtainable from zinc bromide and aniline hydrobromide, separates in thick, colourless plates, is readily soluble in cold water, and does not decompose at 110°.   *Diorthotoluidine zincobromide*,

$$(C_7H_7NH_2)_2,H_2ZnBr_4 + H_2O,$$
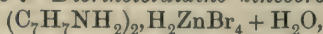
forms large, colourless, prismatic plates which are readily soluble in cold water, and melt and decompose at about 150°.   *Dimetatoluidine zincobromide*, with $2H_2O$, formed in a solution containing an excess of

zinc bromide, is with difficulty separated in a pure state from *trimeta-toluidine zincobromide*, $(C_7H_7NH_2)_3,3HBr,ZnBr_2$, which generally accompanies it; the latter is, however, readily obtained pure from solutions containing an excess of metatoluidine hydrobromide, and crystallises in long, purple needles. *Diparatoluidine zincobromide* separates from solutions of paratoluidine hydrobromide containing an excess of zinc bromide, in thin, lustrous, colourless leaves; on attempting to crystallise it from water, paratoluidine hydrobromide separates.

By mixing solutions of zinc chloride and ammonium chloride in all proportions, only the two salts, $ZnCl_2,2NH_4Cl$ and $ZnCl_2,3NH_4Cl$, described by Marignac (*Ann. des Mines*, 1857, [v], **12**, 1) could be obtained.

Kane has stated (*Annalen*, 1849, **72**, 290) that, on dissolving the compounds $ZnCl_2,NH_3$ and $ZnCl_2,4NH_3$ in hydrochloric acid, corresponding double salts are formed; it appears, however, that the former gives rise to $ZnCl_2,2NH_4Cl$, and the latter to $ZnCl_2,3NH_4Cl$.

A complete bibliography of double chlorides, bromides, iodides, and fluorides of zinc with other metals and with organic bases is appended.   W. A. D.

Schiff's Bases: Diphenamine Compounds of Aliphatic Aldehydes. By ALEXANDER EIBNER (*Annalen*, 1898, **302**, 335—370. Compare von Miller, Plöchl and others, Abstr., 1892, 1189).— Diphenamine compounds are Schiff's bases derived from an aldehyde and two molecular proportions of an amine; ethylidenedianiline, a member of this class, has been recently described by the author (Abstr., 1897, i, 464), and other bases of the same group have been investigated by Eberhardt and Welter (Abstr., 1894, i, 451).

Contrary to the view of the last-named chemists, the presence of alkali is not necessary to the production of diphenamine compounds, which are best prepared by mixing cooled aqueous solutions of alde-hyde and base; in cases where the substances are not soluble in water, solutions in dilute alcohol are employed.

Ethylideneparanitrodiphenamine, $CHMe(NH\cdot C_6H_4\cdot NO_2)_2$, prepared from acetaldehyde and paranitraniline, crystallises in pale-yellow, attenuated needles, and melts at 167°; repeated crystallisation from hot alcohol converts it into paranitraniline. The *nitrile*, $C_9H_9N_3O_2$, obtained by the action of hydrogen cyanide, crystallises from alcohol in golden-yellow needles, and melts at 120°.

Ethylideneparachlorodiphenamine, $CHMe(NH\cdot C_6H_4Cl)_2$, crystallises from a mixture of ether and alcohol in long, colourless needles or plates, and melts at 64—65°; hydrogen cyanide converts it into the *nitrile*, $C_6H_4Cl\cdot NH\cdot CHMe\cdot CN$, which crystallises in leaflets melting at 114·5°, and is also produced when acetaldehyde is added to an ethereal solution of parachloraniline and hydrogen cyanide. The isomeric *nitrile*, obtained on adding chloracetaldehyde to an ethereal solution of aniline and hydrogen cyanide, crystallises from alcohol in quadratic plates, and melts at 83—84°. An attempt to prepare chlorethylidenediphenamine gave rise to a base, containing no halogen, melting at 155°,

Chlorethylideneparachlorodiphenamine, $C_{14}H_{13}N_2Cl_3$, obtained from choracetaldehyde and parachloraniline in ethereal solution, separates in beautiful, lustrous, rhombic crystals when light petroleum is added to the liquid; it melts at 78—79°. A base which melts at 195° is obtained when no medium is employed.

Dichlorethylidenediphenamine, $C_{14}H_{14}N_2Cl_2$, prepared from dichloracetaldehyde and aniline without a diluent, crystallises in rhombic leaflets, and melts at 70—71°; like the foregoing chloro-derivative, it is indifferent towards hydrogen cyanide.

Trichlorethylidenediphenamine, $C_{14}H_{13}N_2Cl_3$, has been described by Wallach; it is prepared from aniline and chloral hydrate, and melts at 107·5°. It is probable that the production of the additive compound, $OH \cdot CHCl_3 \cdot NHPh$, precedes the formation of this substance.

The *additive compound*, $OH \cdot CHCl_3 \cdot NH \cdot C_6H_4Me$, obtained from paratoluidine and chloral, crystallises in colourless, microscopic leaflets, and melts at 75°; *trichlorethylideneparaditolamine*, described by Wallach, melts at 115°, and is obtained from the additive compound by exposure to air, by superfusion, and by treatment with hot water.

The *additive compound*, $OH \cdot CHCl_3 \cdot NH \cdot C_6H_4 \cdot NO_2$, prepared from paranitraniline and chloral, crystallises in aggregates and melts at 128°; when the aldehyde is heated with the base in a reflux apparatus, *trichlorethylideneparanitrodiphenamine*, $C_{14}H_{11}N_4O_4Cl_3$, is produced and melts at 218°.

Trichlorethylidenemetachlorodiphenamine, $C_{14}H_{11}N_2Cl_5$, produced by the action of chloral on metachloraniline in ethereal solution, crystallises from alcohol in slender needles, and melts at 89°; it is very stable, and undergoes no change when exposed to air or boiling water, being volatile in an atmosphere of steam.

Trichlorethylideneparachlorodiphenamine, $C_{14}H_{11}N_2Cl_5$, prepared from chloral and parachloraniline, crystallises from alcohol in short, lustrous prisms, and melts at 143°; it is also very stable, and resists the action of boiling aqueous alkalis.

Trichlorethylidenedichlorodiphenamine, $C_{14}H_9N_2Cl_7$, is obtained by the action of chloral on 2 : 4-dichloraniline, and separates from ether in beautiful, lustrous crystals melting at 144°; it is a remarkably stable substance, resisting the action of boiling alcoholic potash and of boiling acetic anhydride.

Chloral has no action on 1 : 2 : 4 : 6-trichloraniline or on symmetrical dichloronitraniline.   M. O. F.

Action of Nitrous Acid on Secondary Aromatic Amines. By RICHARD STOERMER (*Ber.*, 1898, **31**, 2523—2541).—The question of the manner in which nitro-derivatives are produced by the action of nitrous acid on secondary aromatic amines is discussed at some length. It is found that if a nitrosamine having a nitro-group, or perhaps even a chlorine atom in the para-position, be treated with dilute nitric acid, a nitro-group enters the ring in the ortho-position. In the case of paranitrophenylnitrosamine, by the employment of the quantity of nitric acid theoretically necessary for the conversion of the nitroso- into a nitro-group, it may be almost entirely converted into dinitromethylaniline; the migration of the nitroso-group into

the ring, under the influence of alcoholic hydrochloric or sulphuric acid, was never observed ; on the other hand, paranitromethylaniline does not yield any dinitro-compound under the foregoing conditions. The author concludes that the most plausible view of the sequence of changes is the following : $NO_2 \cdot C_6H_4 \cdot NMe \cdot NO + O = NO_2 \cdot C_6H_4 \cdot NMe \cdot NO_2 = C_6H_3(NO_2)_2 \cdot NHMe$, the latter change being exactly similar to those observed by Bamberger (Abstr., 1893, i, 327, &c.) in the case of other nitramines.

1. [With PAUL HOFFMANN.]—A rapid stream of nitrous acid is passed into methylaniline suspended in water ; after 2 hours, the paranitro-nitrosomethylaniline formed becomes crystalline, and may be separated by filtration ; the substance may also be obtained by the action of nitric peroxide on methylaniline dissolved in cold ether. It is converted into paranitromethylaniline by hot hydrochloric acid, and when heated with dilute nitric acid (1 in 3) affords nearly the theoretical amount of 2 : 4-dinitromethylaniline ; the latter was found to melt at 176—177° (corr.). If the quantity of nitric acid theoretically necessary be employed, the yield obtained is 88·2 per cent. of the possible amount.

Acetoparanitromethylaniline, $NO_2 \cdot C_6H_4 \cdot NMeAc$, produced by heating nitromethylaniline with acetic anhydride in closed tubes at 175° for 14 hours, melts at 152—153°. Gaseous nitrous acid causes replacement of the acetyl by the nitroso-group, and separation of the acetyl group is also effected by dilute nitric acid or alcoholic hydrogen chloride.

Paranitronitrosomethylaniline is not affected by warm hydrogen peroxide, alkaline ferricyanide, or by a solution of chromic anhydride in acetic acid ; it is not altered after remaining in contact with a cold alcoholic solution of hydrogen chloride ($1\frac{1}{2}$ per cent.) for 3 weeks.

2 : 4-*Dinitronitrosomethylaniline*, $C_6H_3(NO_2)_2 \cdot NMe \cdot NO$, made by passing a stream of nitrous acid into a cooled alcoholic solution of 2 : 4-dinitromethylaniline, closely resembles the corresponding mono-nitro-compound in regard to its stability towards different reagents ; it crystallises from hot alcohol in flat, pale yellow needles, and melts at 85—86°.

Paranitronitrosoethylaniline, $NO_2 \cdot C_6H_4 \cdot NEt \cdot NO$, crystallises from hot alcohol in straw-coloured needles and melts at 119—120°. When heated with dilute nitric acid, it yields 2 : 4-dinitroethylaniline ; this was found to melt at 113—114°, and its *nitroso*-derivative, $C_8H_8O_5N_4$, at 51·5—52·5°.

Orthochloromethylaniline is a pale-brown liquid boiling at 215—216° (corr.) under a pressure of 764 mm. ; its sp. gr. = 1·1735 at 11·5° ; its *nitroso*-derivative is a liquid, and has a sp. gr. = 1·266 at 15°. Meta-chloromethylaniline was found to boil at 234·5—235·5° at 764 mm. pressure (compare La Coste and Bodewig, Abstr., 1885, 792), and has a sp. gr. = 1·174 at 11·5° ; its *nitrosamine* forms brown leaflets and melts at 34—35°.

Metachlorethylaniline is a brown liquid and boils at 243—244° at 760 mm. pressure ; its sp. gr. = 1·120 at 19° ; its *nitroso*-compound is an oil having a sp. gr. = 1·227 at 20°. Parachloromethylaniline is oily, boils at 239—240° at 764 mm., and has a sp. gr. = 1·169 at 11·5° ;

the nitroso-derivative crystallises in prisms and melts at 51° (compare Koch, Abstr., 1887, 1041).

4-*Chloromethylorthotoluidine*, obtained from the corresponding chloronitrotoluene, is a colourless liquid which gradually assumes a greenish hue ; it boils at 248·5—249·5° at 760 mm. pressure ; its sp. gr. = 1·138 at 19°. The *nitroso*-derivative is an oil, and has a sp. gr. = 1·226 at 20°.

2 : 4-*Chloronitronitrosomethylaniline*, $C_7H_6O_3N_3Cl$, is obtained by acting on orthochloromethylaniline with nitrous acid ; it forms yellowish-white needles and melts at 94·5—95·5° ; when boiled with strong hydrochloric acid, it yields pure 2 : 4-*chloronitromethylaniline*, $C_7H_7O_2N_2Cl$, which crystallises in small, sulphur-yellow needles and melts at 116—117°.

3-*Chloronitronitrosomethylaniline*, $C_7H_6O_3N_3Cl$, prepared by the long-continued action of nitrous acid on metachloromethylaniline, crystallises from hot alcohol in light-brown prisms and melts at 67·5—68·5°. 3-*Chloronitromethylaniline*, $C_7H_7O_2N_2Cl$, forms canary-yellow needles, and melts at 106—107°.

3-*Chloronitronitrosoethylaniline*, $C_8H_8O_3N_3Cl$, crystallises in small, yellow needles and melts at 75·5—76·5° ; 3-*Chloronitroethylaniline*, $C_8H_9O_2N_2Cl$, in yellow needles and melts at 75·5—76·5°.

4 : 3(?)-*Chloronitronitrosomethylorthotoluidine*, $C_8H_8O_3N_3Cl$, crystallises from alcohol in large, thick, pale yellow leaflets and melts at 80·5—81·5°. The corresponding *chloronitromethyltoluidine*, $C_8H_9O_2N_2Cl$, crystallises from alcohol in slender, bright yellow needles and melts at 185—186° ; on reduction with tin and hydrochloric acid, it yields a *diamine* which crystallises in brownish needles, melts at 85°, and when treated in hydrochloric acid solution with hydrogen sulphide and ferric chloride, affords a beautiful violet coloration, hence the base is probably a *paradiamine*.

4 : 2 : 6-*Chlorodinitronitrosomethylaniline*, $C_7H_5O_5N_4Cl$, is obtained in the usual manner from parachloromethylaniline, and is accompanied by 4 : 2-chloronitromethylaniline ; it crystallises in flat, white needles, and melts at 99—99·5°. The corresponding *chlorodinitromethylaniline*, $C_7H_6O_4N_3Cl$, forms beautiful orange needles and melts at 100—100·5°.

3 : 5-*Dinitronitrosomethylorthotoluidine* crystallises in beautiful, shining, yellowish rhombohedra and melts at 94—95°. The corresponding dinitromethyltoluidine has already been obtained by Bamberger and Seitz (Abstr., 1897, i, 466).

Nitronitrosomethylmetatoluidine, $C_8H_9O_3N_3$ [Me : N(NO)Me : NO_2 = 1 : 3 : 6(?)], forms elongated, yellowish leaflets and melts at 73—74°. The corresponding *nitromethyltoluidine*, $C_8H_{10}O_2N_2$, crystallises in yellowish-brown leaflets having a blue reflex, and melts at 92—93°.

Paranitronitrosodiphenylamine is readily obtained in quantitative amount by passing nitrous anhydride for 20 minutes through an ice cold solution of diphenylamine (5 grams) in alcohol (20—25 c.c.) ; it melts at 133—134°. If the action of the gas be prolonged (3 hours), an orange, crystalline mass, sparingly soluble in alcohol and melting at 156—170°, is formed (compare Meldola, *Ber.*, 1878, 11, 351). The nitronitroso-compound is also readily obtained by adding a few drops of nitric peroxide to a solution of nitrosodiphenylamine in dry carbon

bisulphide. If a solution in chloroform is used, separation of symmetrical *paradinitrodiphenylamine*, $NH(C_6H_4 \cdot NO_2)_2$, occurs after 2 hours; this substance crystallises from hot alcohol in yellow needles having a blue shimmer, and melts at 214—214·5°. Under certain conditions, orthoparadinitrodiphenylamine (m. p. = 156·5—157°) is formed in small quantity, and also a *trinitrodiphenylamine*, $C_{12}H_8N_4O_6$, melting at 170—173°. Paranitronitrosodiphenylamine yields paradinitrodiphenylamine by the action of dilute nitric acid.

[With Kurt Dragendorff.]—When nitrous acid acts on tetrahydroquinoline dissolved in water or alcohol, a product is obtained which, when roughly purified, melts at 137—138° (compare Hoffmann and Königs, Abstr., 1883, 1143), but which in reality consists of two substances, one crystallising in beautiful, shining needles and melting at 154—155°, and the other forming red-brown needles and melting at 99—100°; the former is probably *4-nitro-1'-nitrosotetrahydroquinoline*, $NO_2 \cdot C_9NH_9 \cdot NO$, and the latter the corresponding *2-nitro*-compound. Both yield the respective nitrotetrahydroquinolines on treatment with hydrochloric acid, but the para-derivative does not give a dinitrocompound on treatment with dilute nitric acid.

4-Nitrotetrahydroquinoline, $C_9H_{10}O_2N_2$, forms dark yellow needles having a bluish metallic sheen, and melts at 163—164°. *2-Nitrotetrahydroquinoline*, $C_9H_{10}N_2O_2$, crystallises in shining, red needles and melts at 82—83°. Both of these are feeble bases, dissolving in acids, and being reprecipitated on addition of water.

1-Nitro-1'-nitroso-3-methyltetrahydroquinoline, $C_{10}H_{11}O_3N_3$, produced by the action of nitrous anhydride on tetrahydroquinoline, forms beautiful, yellow needles and melts at 122°. It is accompanied by two other substances. The first of these is the corresponding 1-nitrotetrahydro-3-methylquinoline, $C_{10}H_{12}O_2N_2$; it forms beautiful, dark red, rectangular tables and melts at 103—105°; it is also obtained by hydrolysis of the nitronitroso-compound with boiling alcohol. The second substance is probably a *2 (or 4)-nitro-3-methyltetrahydroquinoline*, $C_{10}H_{12}O_2N_2$; it crystallises in long, yellowish, feathery needles, melts at 67°, and is a stronger base than its isomeride.

3-Nitro-1-nitroso-1-methyltetrahydroquinoline, $C_{10}H_{11}O_3N_3$, forms small, bright-yellow needles, melts at 100—102°, and dissolves sparingly in alcohol, but readily in a mixture of alcohol and benzene. The corresponding *3-nitro-1-methyltetrahydroquinoline*, $C_{10}H_{12}N_2O_2$, forms dark-yellow crystals having a bluish, metallic sheen and melts at 142°; it dissolves readily in alcohol.

When nitrous anhydride is led into an alcoholic solution of tetrahydroquinaldine, Müller's nitronitrosotetrahydroquinaldine (m. p. = 152—153°) is formed, and is accompanied by a small quantity of *1(?)-nitronitrosotetrahydroquinaldine*, $C_{10}H_{11}N_3O_3$, which melts at 105—107°. 3-Nitrotetrahydroquinaldine, $C_{10}H_{12}O_2N_2$, forms dark, brownish-red crystals having a metallic lustre, and melts at 130—132°.

Two isomeric nitronitroso-derivatives, $C_9H_9O_3N_3$, may be obtained from hydromethylketole. One, probably the *1-nitro*-compound, forms dark yellow crystals and melts at 108°; the second, doubtless the *paranitro*-derivative, separates in yellow crystals and melts at 135°.

3-*Nitrohydroketole*, $C_9H_{10}O_2N_2$, forms brown needles with a beautiful, metallic lustre and melts at 82°.

3-*Nitro*-1'-*nitrosohydro*-2'-*phenylindole*, $C_{14}H_{11}O_3N_3$, is obtained in bright yellow, shining crystals and melts at 160°. It was not accompanied by any isomeride, and did not yield any crystalline product on hydrolysis.   A. L.

Thionyl Compounds of Substituted Paraphenylenediamines. By A. Francke (*Ber.*, 1898, **31**, 2179—2182. Compare Abstr., 1893, i, 518; and 1898, i, 431).—*Thionylparamidodimethylaniline*, $NMe_2 \cdot C_6H_4 \cdot N\!:\!SO$, is obtained by treating amidodimethylaniline with thionyl chloride in benzene solution; it is dark red with a greenish surface lustre, and melts at 72°. In the air, it becomes converted gradually into the yellow thionamic acid, $NMe_2 \cdot C_6H_4 \cdot NH \cdot SO_2H$, which is more readily obtained by passing sulphurous anhydride into an ethereal solution of amidodimethylaniline. With benzaldehyde in alcoholic solution, this acid yields a *compound*,

$$NMe_2 \cdot C_6H_4 \cdot N(SO_2H) \cdot CHPh \cdot OH,$$
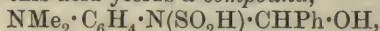
which is white, melts at 150°, and when heated, or treated with alkalis, forms parabenzylideneamidodimethylaniline, $NMe_2 \cdot C_6H_4 \cdot N\!:\!CHPh$. When thionylamidodimethylaniline is heated with dimethylaniline and zinc chloride in a sealed tube at 100°, some methylene-blue is formed, but only in very small amount.

Thionylparamidodiethylaniline, $NEt_2 \cdot C_6H_4 \cdot N\!:\!SO$, melts at 36°; the *hydrochloride* melts at 170°, and is decomposed by water; the thionamic acid melts at 122—124°.

Paramidomethylbenzylaniline, prepared by reducing nitrosomethylbenzylaniline, boils at 290—295°; *thionylparamidomethylbenzylaniline*, $CH_2Ph \cdot NMe \cdot C_6H_4 \cdot N\!:\!SO$, melts at 94°.

Thionylamidodiphenylamine, $NHPh \cdot C_6H_4 \cdot N\!:\!SO$, melts at 142°, and is fairly stable.

Thionyl-1-*amidodinaphthylamine*, $C_{10}H_7 \cdot NH \cdot C_{10}H_6 \cdot N\!:\!SO$, melts at 120°, and is the most stable of all these compounds.   C. F. B.

Condensation of Amidoguanidine with Aromatic Aldehydes and Ketones. By Johannes Thiele and Richard Bihan (*Annalen*, 1898, **302**, 299—311. Compare Abstr., 1892, 1297).—Aqueous solutions of an amidoguanidine salt are agitated with an aldehyde or its alcoholic solution, when one drop of a mineral acid induces condensation. *Orthohydroxybenzylideneamidoguanidine*,

$$OH \cdot C_6H_4 \cdot CH\!:\!N \cdot NH \cdot C(NH_2)\!:\!NH,$$
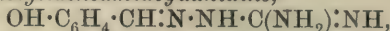
crystallises from chloroform in lustrous leaflets and melts at 102°; the *nitrate* and *hydrochloride* crystallise in long needles, and melt at 209—210° and 215—216° respectively. Protracted treatment with boiling alkali converts the substance into orthohydroxybenzylideneazine, obtained by Curtius and Pflug from hydrazine and salicylaldehyde. *Parahydroxybenzylideneamidoguanidine* crystallises from water in plates containing $1H_2O$ and melts at 204°; the *nitrate* melts and decomposes at 216°.

Orthonitrobenzylideneamidoguanidine,

$$NO_2 \cdot C_6H_4 \cdot CH\!:\!N \cdot NH \cdot C(NH_2)\!:\!NH,$$
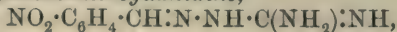
crystallises in long, orange-yellow needles and melts at 185°; the *nitrate* melts and decomposes at 251°. *Metanitrobenzylideneamidoguanidine* crystallises in yellow, highly refractive needles, which melt and decompose at 210°; the *nitrate* melts at 247°. Paranitrobenzylidineamidoguanidine has been described by Wedekind (Abstr., 1897, i, 241); the *nitrate* melts and decomposes at 241°. The paranitro-compound contains $1H_2O$, and melts at 198° (Wedekind gives 206°); it is produced along with the ortho-derivative when benzylideneamidoguanidine nitrate is added to concentrated sulphuric acid.

The *diacetyl* derivative of benzylideneamidoguanidine crystallises from water, and melts at 158—159°.

Benzylidenemethylhydroxypyrimidinehydrazine,

$$CH \diagdown^{CMe---N}_{C(OH):N} \diagup C \cdot NH \cdot N : CHPh,$$
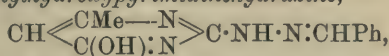
prepared from benzylideneamidoguanidine and ethylic acetoacetate, crystallises from alcohol; it contains $1H_2O$, and melts at 232—233°. Boiling hydrochloric acid eliminates benzaldehyde, and gives rise to hydrazine and methyluracil, described by Behrend.

Diphenylamidotriazine, $N \diagdown^{CPh---CPh}_{N:C(NH_2)} \diagup N$, obtained from amidoguanidine nitrate and benzil, crystallises from alcohol, and melts at 175°; the *acetyl* derivative melts at 151°.

Amidophenantriazine, $\begin{array}{l} C_6H_4 \cdot C : N \cdot N \\ C_6H_4 \cdot C : N \cdot C NH_2 \end{array}$, prepared from amidoguanidine and phenanthrenequinone, crystallises from alcohol in pale yellow needles and melts at 262°.   M. O. F.
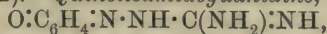
Condensation of Amidoguanidine and of Semicarbazide with Quinones. By JOHANNES THIELE and WILLY BARLOW (*Annalen*, 1898, 302, 311—332).—*Quinoneamidoguanidine,*

$$O:C_6H_4:N \cdot NH \cdot C(NH_2):NH,$$

forms slender, cherry-red needles, soluble in hot water, but dissolving sparingly in alcohol and ether; it begins to decompose at 208°, and melts at 212—215°. Excess of boiling caustic potash eliminates ammonia and gives rise to phenol. The *nitrate*, prepared by heating amidoguanidine nitrate (1 mol.) with alcoholic quinone in a reflux apparatus, crystallises from water in slender, orange-yellow needles; it melts and decomposes at about 186°. The *hydrochloride* forms red crystals melting at about 173°, and the *picrate* crystallises in yellow needles, and melts with previous decomposition at 232°; the *potassium* derivative crystallises in golden-yellow leaflets, and becomes red and absorbs moisture when exposed to air. The *hydrochloride* of dihydroquinoneamidoguanidine, $OH \cdot C_6H_4 \cdot NH \cdot NH \cdot C(NH_2):NH,HCl$, forms colourless crystals and melts at 208°.

Quinonebisamidoguanidine, $C_6H_4[:N \cdot NH \cdot C(NH_2):NH]_2$, crystallises in cherry-red needles and melts at 250°, decomposing somewhat below this temperature; boiling aqueous potash eliminates ammonia, and gives rise to a small proportion of phenylhydrazine. The *nitrate*, obtained from amidoguanidine nitrate (2 mols.) and quinone, crystallises in yellow needles, and does not melt below 280°; the *hydrochloride* forms needles, and also remains unfused at 280°. The *hydrochloride*

of dihydroquinonebisamidoguanidine,

$$C_6H_4[\cdot NH\cdot NH\cdot C(NH_2)\dot:NH]_2,2HCl,$$
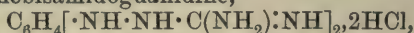
forms colourless crystals and melts at 223°.

α-Naphthaquinoneamidoguanidine, $O\dot:C_{10}H_6\cdot N\cdot NH\cdot C(NH_2)\dot:NH$, dissolves with great difficulty in water, but is more freely soluble in alcohol; it decomposes at 222°, and melts at about 233°. The *nitrate* forms slender, yellow needles, and melts at about 253°, whilst the *hydrochloride* decomposes at about 235°; the *sulphate* decomposes at 260°, and the *picrate* melts indefinitely at about 272°.

*α-Naphthaquinonebisamidoguanidine*, $C_{10}H_6[\dot:N\cdot NH\cdot C(NH_2)\dot:NH]_2$, crystallises in orange-yellow needles, and decomposes when its solutions are evaporated; on heating the substance with alkalis, naphthalene is produced, and naphthylhydrazine is not among the products. The *nitrate*, forming yellowish-green needles, does not melt below 277°; and the *sulphate*, which crystallises from water in yellow needles containing $1H_2O$, melts at 260°, previously undergoing decomposition.

β-Naphthaquinoneamidoguanidine decomposes and sublimes at 175—180°, and melts at about 202°; the *nitrate* and *hydrochloride* crystallise in orange yellow needles, and decompose at 217° and 278° respectively. When the base is heated with aqueous potash, *α*-naphthol and the *compound* $C_{11}H_7N_3O$ are formed; the latter crystallises from its solution in alcohol, which has a red colour and exhibits green fluorescence, and yields *sodium* and *silver* derivatives. The *hydrochloride* of dihydro-*β*-naphthaquinoneamidoguanidine,

$$OH\cdot C_{10}H_6\cdot NH\cdot NH\cdot C(NH_2)\dot:NH,HCl,$$
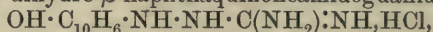
forms colourless needles containing $1H_2O$.

The *nitrate* of nitroso-*β*-naphtholamidoguanidine,

$$NOH\dot:C_{10}H_6\dot:N\cdot NH\cdot C(NH_2)\dot:NH,HNO_3,$$
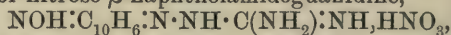
melts at about 145°, and yields no precipitate with ammonia. The *compound*, $C_{11}H_8N_4O$, obtained by the elimination of the elements of ammonium nitrate through the agency of boiling water, separates from alcohol in yellow crystals, and melts above 240°; the *hydrochloride* forms compact, red crystals, and the *nitrate* is decomposed by water. Reduction with stannous chloride and hydrochloric acid renders the substance colourless, yielding the crystalline *hydrochloride*, $C_{11}H_{10}N_4,HCl$, which melts and decomposes at 225°; ferric chloride liberates from this salt the *compound*, $C_{11}H_8N_4$, which crystallises from alcohol in needles melting at 201°, and forms a *hydrochloride* and *nitrate*.

Quinonesemicarbazone, $O\dot:C_6H_4\dot:N\cdot NH\cdot CO\cdot NH_2$, prepared from alcoholic quinone and semicarbazide hydrochloride (1 mol.), crystallises from petroleum in small, yellow needles, and melts at 172°; it dissolves readily in alkalis, which, on boiling, give rise to phenol. *Quinonedisemicarbazone*, $C_6H_4(\dot:N\cdot NH\cdot CO\cdot NH_2)_2$, forms a fine, red, crystalline powder, and melts at about 243°; boiling alkalis produce phenylhydrazine.

α-Naphthaquinonesemicarbazone, $O\dot:C_{10}H_6\dot:N\cdot NH\cdot CO\cdot NH_2$, separates from glacial acetic acid in greenish-yellow crystals melting at 247° after undergoing decomposition; alkalis give rise to *α*-naphthol. *β-Naphthaquinonesemicarbazone* crystallises from alcohol in golden-yellow leaflets, and decomposes at 184°.

Quinoneoximesemicarbazone, $NOH\dot:C_6H_4\dot:N\cdot NH\cdot CO\cdot NH$, crystallises

in slender, brownish-yellow needles when the solution in glacial acetic acid is poured into much water; it decomposes at about 238°.

Nitroso-β-naphtholsemicarbazone, $NOH\!:\!C_{10}H_6\!:\!N\!\cdot\!NH\!\cdot\!CO\!\cdot\!NH_2$, forms yellow needles and melts at about 189°. M. O. F.

History of Phenylhydroxylamine. By ALFRED WOHL (*Ber.*, 1898, **31**, 2543).—The author repeats his claim to priority (Abstr., 1894, i, 409) in the discovery of phenylhydroxylamine. A. L.

Regularities of Substitution in the Formation of Azo-colouring Matters. By JOHANNES PINNOW and A. MATCOVITCH (*Ber.*, 1898, **31**, 2514—2523. Compare Abstr., 1896, i, 161 and 427). —*Diamidodimethylparatoluidine*, $C_9H_{15}N_3$, is obtained by reducing the product of interaction of orthamidodimethylparatoluidine and diazobenzenesulphonic acid with stannous chloride and hydrochloric acid; it boils at 193·5° (uncorr.) under 40 mm. pressure, and melts, after sintering slightly, at 60—61°. The *picrate*, $C_9H_{15}N_3,2C_6H_3N_3O_7$, forms brilliant, rhombohedral, yellowish-brown tables, melts at 157—158°, dissolves readily in acetone and hot water, less readily in cold alcohol, ethylic acetate, and chloroform, and only sparingly in ether or benzene; it is insoluble in light petroleum. The *hydrobromide* crystallises in tables, and dissolves very readily in water and alcohol. The *diacetyl* derivative, $C_{13}H_{19}N_3O_2$, forms rhombic tables and melts at 235—236°.

2-Acetamido-3 : 1′ : 2′-trimethylbenzimidazole,

$$NHAc\cdot C_6H_2Me\!\!<\!\!\genfrac{}{}{0pt}{}{NMe}{\underline{\quad}N}\!\!\!>\!\!CMe,$$
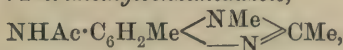
produced when diamidodimethylparatoluidine is heated with acetic anhydride under pressure at 154—158°, crystallises from water or alcohol in prisms, or slender, shining needles, and melts at 237—238°. As the production of this substance from amidodimethyltoluidine is attended with the loss of a methyl group, it follows that an amido-group in the parent substance is in the ortho-position relatively to the dimethylamido-group. The *picrate*, $C_{12}H_{15}N_3O,C_6H_3N_3O_7$, forms small, sulphur-yellow needles, melts at 264°, dissolves readily in hot acetic acid, ethylic acetate, and alcohol, but only sparingly in the cold solvents and in acetone. *2-Amido-3 : 1′ : 2′-trimethylbenzimidazole*, $C_{10}H_{13}N_3$, prepared from the acetyl derivative by hydrolysis with hot hydrochloric acid, crystallises in slender needles, melts at 237—237·5°, and dissolves in most organic media, with the exception of ether and light petroleum. The *hydrochloride*, $C_{10}H_{13}N_3,2HCl$, crystallises from hydrochloric acid in anhydrous needles, and does not melt below 295°. The *picrate*, $C_{10}H_{13}N_3,C_6H_3N_3O_7$, forms a dense, bright yellow, crystalline powder and melts and effervesces at 265°; it is somewhat readily soluble in hot acetic acid, but is sparingly soluble in the cold liquid and in the usual organic solvents. *3 : 1′ : 2′-Trimethylbenzimidazole-2-azo-β-naphthylamine*, $C_{20}H_{19}N_5$, crystallises from alcohol in slender, yellowish-red prisms and melts and decomposes at 254—257°; it dissolves readily in acetic acid and hot ethylic acetate, but is only sparingly soluble in acetone and ether.

Metadinitrodimethylparatoluidine, $C_9H_{11}N_3O_4$, obtained from dinitroparatoluidine by the action of a large excess of dilute nitric and

sulphuric acids at 15—17°, crystallises from light petroleum in thick, red needles, melts at 95°, and dissolves readily in the usual organic media, with the exception of cold alcohol and light petroleum. Its constitution follows from the fact that it yields metadinitrotolylmethylnitramine under the influence of fuming nitric acid. *Acetamidonitrodimethylparatoluidine*, $C_{11}H_{15}N_3O_3$, is made from the foregoing compound by reduction with alcoholic ammonium sulphide, followed by treatment with acetic anhydride; it crystallises from light petroleum in bright yellow needles and melts at 97°.

Metadiamidodimethylparatoluidine, $C_9H_{15}N_3$, obtained by reducing dinitrodimethyltoluidine with tin and hydrochloric acid, crystallises from light petroleum in long, white, striated needles, melts at 54·5—56·5°, and boils at 189° under 22 mm. pressure. The *hydrochloride*, $C_9H_{15}N_3,2HCl$, crystallises from hydrochloric acid in needles or prisms, melts at 221—225°, and is less readily soluble in water and hydrochloric acid than its isomeride. The *picrate*, $C_9H_{15}N_3,2C_6H_3N_3O_7$, forms thick, sulphur-yellow needles, and melts at 142—143°. The *diacetyl* derivative, $C_{13}H_{19}N_3O_2$, crystallises from ethylic acetate in bundles of long needles, and melts at 151—152°.

1-*Acetamido*-3 : 1′ : 2′-*trimethylbenzimidazole*, produced on heating diamidodimethylparatoluidine with acetic anhydride in sealed tubes, crystallises in long, slender needles from methylic alcohol, and in this state has the composition $2C_{12}H_{15}N_3O + MeOH$; it melts at 199—201°. The *picrate*, $C_{12}H_{15}N_3O,C_6H_3N_3O_7$, separates from glacial acetic acid in bundles of sulphur-yellow needles and melts at 158—159·5°. 1-*Amido*-3 : 1′ : 2′-*trimethylbenzimidazole*, $C_{10}H_{13}N_3$, crystallises from methylic alcohol in needles which have the composition $2C_{10}H_{13}N_3 + MeOH$; it melts at 129—130°, dissolves readily in hot acetone and methylic alcohol, and moderately readily in the cold liquids and hot water. The *hydrochloride*, $C_{10}H_{13}N_3,2HCl$, crystallises in rectangular plates and does not melt below 285°. The *picrate*, $C_{10}H_{13}N_3,C_6H_3N_3O_7$, melts at 224—225°. 3 : 1′ : 2′-*Trimethylbenzimidazole*-1-*azo*-β-*naphthylamine*, $C_{20}H_{19}N_5$, forms red prisms having a green surface colour and melts at 258—259°.

The *compound*, $C_{15}H_{18}N_4SO_3$, obtained when metamidodimethylparatoluidine is treated with diazobenzenesulphonic acid, forms a readily dissociated acetate which crystallises from alcohol in cube-like forms and melts at 205—206°; on hydrolysis, it yields diamidodimethylparatoluidine which boils at 198—202° and forms a diacetyl derivative; the latter crystallises from methylic alcohol in rhombic tables and melts at 234·5—236°. These compounds and the corresponding acetamidotrimethylbenzimidazole are identical with those obtained in a similar manner from orthamidodimethylparatoluidine; it follows that when diazobenzenesulphonic acid acts on metamidodimethylparatoluidine, it is the hydrogen in the meta-position with regard to the dimethylamido-group which is replaced, hence the dimethylated amidogroup exercises no directive influence on the substitution.   A. L.

Formation of Phenylhydrazides by the action of Phenylhydrazine on Organic Acids in the Cold. By VIRGIL L. LEIGHTON (*Amer. Chem. J.*, 1898, **20**, 676—679).—On dissolving

phenylhydrazine in a slight excess of cold formic acid, and allowing the solution to stand during 24 hours, 71·7 per cent. of the theoretical amount of formophenylhydrazide is obtained. Cold acetic and propionic acids act more slowly on phenylhydrazine, 61 per cent. of the theoretical amount of β-acetophenylhydrazide being produced during 4 days in the former, and 86·6 per cent. of propiono-phenylhydrazide during 5 days in the latter case.

A 25 per cent. yield only of *isobutyrophenylhydrazide*, $N_2H_2Ph\cdot COPr^\beta$, was obtained from cold isobutyric acid and phenylhydrazine after 7 days; the hydrazide is nearly insoluble in water, and crystallises from alcohol in rectangular or hexagonal plates and melts at 142—143°.

Forty-seven per cent. of the theoretical amount of *isohexophenyl-hydrazide*, $N_2H_2Ph\cdot CO\cdot C_5H_{11}$, is formed from cold isohexoic acid during 5 days; it separates from light petroleum in thin, transparent crystals and melts at 144—145°.

From heptoic acid, 86·4 per cent. of the *heptophenylhydrazide*, $N_2H_2Ph\cdot CO\cdot C_6H_{13}$, required by theory is formed during 6 days, the latter crystallises from alcohol in thin, transparent prisms and melts at 103—104°.

In acetic acid, as in aqueous solution, 1-phenyl-5-pyrazolone-3-carboxylic acid is formed by the action of phenylhydrazine on acetylenedicarboxylic acid; in presence of an excess of the hydrazine, however, a totally different crystalline *substance* is obtained, which is being investigated by the author. W. A. D.

Orthohydroxyguanazyl Benzene. By EDGAR WEDEKIND (*Ber.*, 1898, **31**, 2353—2354. Compare Abstr., 1898, i, 453).—The free base *orthohydroxybenzylideneamidoguanidine*, obtained by saturating an alkaline solution of amidoguanidine nitrate and salicylaldehyde with carbonic anhydride, forms colourless needles, melts at 100—102°, and dissolves easily in warm water, alcohol, chloroform, and benzene, and sparingly in ether and petroleum.

Orthohydroxyguanazylbenzene,

$$NH_2\cdot C(NH)\cdot NH\cdot N\!:\!C(C_6H_4\cdot OH)\cdot N_2Ph,$$
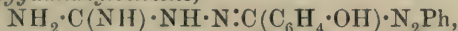
produced by adding a solution of diazobenzene chloride, neutralised with caustic soda, to a dilute alcoholic solution of the above base, crystallises from alcohol in light yellow prisms, and melts at 191—192°, is soluble in the usual organic solvents, and develops an intense yellowish-red coloration with solutions of the alkalis.

G. T. M.

Action of Cyanamide on Chloranil in presence of Potassium Hydroxide. By H. IMBERT (*Compt. rend.*, 1898, **126**, 1879—1882).—When 4 molecular proportions of potassium hydroxide are added to a boiling aqueous solution of cyanamide (2 mols.) containing finely-powdered chloranil (1 mol.) in suspension, the compound $CN_2\!:\!C_6Cl_2(OK)_2\!:\!CN_2 + 2H_2O$ is obtained, and crystallises from water in brownish-green needles with a metallic lustre. It becomes anhydrous at 105°. The silver salt is brown, insoluble, and anhydrous.

When the potassium salt is boiled with excess of potassium

hydroxide, ammonia is liberated, and potassium carbonate and potassium chloranilate are formed. It follows that the product of the action of potassium hydroxide and cyanamide on chloranil differs from chloranilic acid in containing two CN_2-groups in place of the quinonic oxygen atoms. The hydrogen compound, $CN_2 : C_6Cl_2(OH)_2 : CN_2$, seems to form bluish-black crystals, but has not yet been isolated in a pure state. Under certain conditions, the action of concentrated hydrochloric acid on the potassium compound yields a precipitate and liberates a gas; the precipitate seems to be a mixture of the compound $CN_2 : C_6Cl_2(OH)_2 : O$ with a condensed product of the nature of an acetal (compare Abstr., 1898, i, 411).   C. H. B.

Phenylurethanes derived from the Ethereal Salts and Nitriles of some Hydroxy-acids. By Eugène Lambling (*Compt. rend.*, 1898, 127, 64—67).—*Ethylic lactate phenylurethane,*

$$COOEt \cdot CHMe \cdot O \cdot CO \cdot NHPh,$$
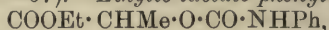
obtained by heating at 180° a mixture of ethylic lactate with phenyl-carbimide in molecular proportion, is a brown oil which cannot be crystallised, and decomposes, when distilled under diminished pressure, with formation of diphenylcarbamide. When treated with 10 per cent. soda in the cold, it is converted into *sodium lactate phenyl-urethane,* which crystallises from alcohol in microscopic prisms, and this, with dilute hydrochloric acid, yields the corresponding *acid,* which crystallises in microscopic tablets melting at 139—140°; this is slightly soluble in water, readily soluble in sodium carbonate solution, alcohol, and ether, and less soluble in chloroform, from which it crystallises in fine needles. *Ethylic trichlorolactate phenylurethane,* $COOEt \cdot CH(CCl_3) \cdot O \cdot CO \cdot NHPh$, from ethylic trichlorolactate and phenylcarbimide, crystallises from a mixture of ether with light petroleum in needles melting at 57·5°; it is slightly soluble in water, and soluble in organic solvents. On treatment with soda, it yields an internal anhydride which will be described hereafter. *Trichlorolacto-nitrile phenylurethane,* $CCl_3 \cdot CH(CN) \cdot O \cdot CO \cdot NHPh$, obtained by heat-ing a mixture of chloral cyanhydrate with phenylcarbimide at 130—140°, crystallises in hexagonal tablets melting at 115—116° and is soluble in organic solvents. *Ethylic glycollate phenylurethane,* $COOEt \cdot CH_2 \cdot O \cdot CO \cdot NHPh$, the preparation of which is similar to that of the preceding compounds, crystallises in microscopic prisms melting at 65°; it is fairly soluble in boiling water, more so in alcohol and ether. When boiled with soda, a solution is obtained from which hydrochloric acid precipitates *glycollic acid phenylurethane* in quadrangular tablets melting at 134—135°, and soluble in alcohol and ether. *Glycollonitrile phenylurethane,* $CN \cdot CH_2 \cdot O \cdot CO \cdot NHPh$, crystallises from a mixture of ether with light petroleum in stellate groups of microscopic prisms melting at 74—75°. *Ethylic phenylglycollate phenylurethane,* $COOEt \cdot CHPh \cdot O \cdot CO \cdot NHPh$, crystal-lises in cauliflower-like masses of microscopic needles melting at 93°, and soluble in alcohol, ether, and chloroform. When treated with the theoretical quantity of soda, it at first dissolves, and then gives a crystalline precipitate of phenylglycolanilide, $OH \cdot CHPh \cdot CO \cdot NHPh$, a substance already obtained by Haller; the mother liquor, on

adding hydrochloric acid, yields *phenylglycollic acid phenylurethane*, which crystallises in microscopic needles. *Phenylglycollonitrile phenylurethane*, $CN \cdot CHPh \cdot O \cdot CO \cdot NHPh$, crystallises from a mixture of ether with light petroleum in microscopic prisms melting at 105°. *Ethylic β-hydroxybutyrate phenylurethane*, $COOEt \cdot CH_2 \cdot CHMe \cdot O \cdot CO \cdot NHPh$, was obtained as a reddish-brown oil, insoluble in water but soluble in alcohol and ether, which could not be distilled or crystallised. *Ethylic α-hydroxyisobutyrate phenylurethane*, $COOEt \cdot CMe_2 \cdot O \cdot CO \cdot NHPh$, crystallises from a mixture of light petroleum with a little ether, in long, silky needles melting at 77·5°, soluble in chloroform, very soluble in alcohol and ether. When boiled for a short time with the theoretical quantity of soda, a solution is obtained which, on cooling, deposits glistening scales of α-hydroxyisobutyranilide, $OH \cdot CMe_2 \cdot CO \cdot NHPh$, a compound already prepared by Tigerstedt. The mother liquor from these crystals, when acidified with hydrochloric acid, yields microscopic needles of *α-hydroxyisobutyric acid phenylurethane*, which melt at 130°, and are soluble in alcohol and ether, less so in chloroform.

It appears, from the formation of the compounds described, that the groups CN, Ph, CO, and CCl_3 exercise no perceptible influence on the interaction of the neighbouring hydroxyl with phenylcarbimide, and it would also seem that the latter acts as readily on tertiary as on primary and secondary hydroxyl groups. This is confirmed by its action on tertiary butylic and tertiary amylic alcohols. The phenylurethanes, which were produced in nearly the theoretical amount, crystallised respectively in silky needles melting at 134—135°, and in microscopic prisms melting at 42°. N. L.

Orthophenylthiohydantoic Acid. By RIZZO NICCOLÒ (*Gazzetta*, 1898, **28**, ii, 68—71).—In continuation of his work on Jäger's phenylthiohydantoic acid (Abstr., 1898, i, 659), the author has examined the orthophenylthiohydantoic acid which P. Mayer obtained by the interaction of phenylthiocarbamide with ammonium chloracetate, and finds that it has the constitution, $NHPh \cdot C(NH)S \cdot CH_2 \cdot COOH$, assigned to it by Mayer.

When treated with potash and benzoic chloride, the acid yields benzoylphenylcyanamide, whilst potash alone converts the acid into phenylcyanamide. Orthophenylthiohydantoic acid is soluble in caustic alkalis, but not in alkali carbonates; it may therefore possibly be an internal salt of the constitution $\begin{array}{l} C(NH) \cdot S \cdot CH_2 \\ NH_2Ph \cdot O \cdot CO \end{array}$. W. J. P.

Salol-*O*-phosphinic Acid. By AUGUST MICHAELIS and W. KERKHOF (*Ber.*, 1898, **31**, 2172—2179).—Salol (1 mol.) reacts vigorously with phosphoric chloride ($1\frac{1}{3}$ mols.), and the product, after being purified by treatment with sulphurous anhydride and warming under diminished pressure to expel the thionyl chloride and phosphorus oxychloride that is formed, leaves *salol-O-tetrachlorophosphine*,

$$COOPh \cdot C_6H_4 \cdot O \cdot PCl_4 ;$$
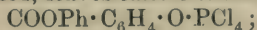
this melts at 44°, and is unusually stable in the presence of water. A bye-product in the reaction, when the latter is too violent, is *phenylic orthochlorobenzoate*, $C_6H_4Cl \cdot COOPh$, which may be obtained readily,

together with phosphorus oxychloride, by heating the phosphine at 180—200°; it melts at 37°. When the phosphine is treated for several hours with sulphurous anhydride at 130—135°, thionyl chloride and *salol-O-oxychlorophosphine*, $COOPh \cdot C_6H_4 \cdot O \cdot POCl_2$, are formed; the latter melts at 70—71°, and boils, decomposing slightly, at 125—135° under 13 mm. pressure. When the tetrachlorophosphine is dissolved in benzene and treated with a little water, *salol-O-phosphinic acid*, $COOPh \cdot C_6H_4 \cdot O \cdot PO(OH)_2 + H_2O$ (the water is lost over sulphuric acid or at 58—60°), is formed; this melts at 62°, or when anhydrous at 88°. It is decomposed by hot alkalis into phenol, salicylic acid, and phosphoric acid; by cold alkalis, into phenol and *salicyl-O-phosphinic acid*; by hot water, or not too dilute acids, into salol and phosphoric acid. The *silver* salt, $COOPh \cdot C_6H_4 \cdot O \cdot P(OAg)_4$, and *lead* salt, $COOPh \cdot C_6H_4 \cdot OPO{:}O_2Pb$, were prepared and analysed, as also the *aniline* salt, $COOH \cdot C_6H_4 \cdot O \cdot PO(OH) \cdot ONH_3Ph$, and the analogous *phenylhydrazine* salt, which melt at 161° and 141° respectively. *Diethylic salol-O-phosphinate*, $COOPh \cdot C_6H_4 \cdot O \cdot PO(OEt)_2$, prepared by heating the tetrachlorophosphine with sodium ethoxide suspended in benzene, boils at 105—115° under 13 mm. pressure; the *diphenylic* salt, prepared in an analogous manner, melts at 76—77°. By treating the tetrachlorophosphine with aniline, *salol-O-phosphinic dianilide*, $COOPh \cdot C_6H_4 \cdot O \cdot PO(NHPh)_2$, melting at 174—175°, is formed; the *diparatoluidide* and *diphenylhydrazide*, prepared in a similar manner, melt at 146° and 170° respectively. An *oxyphosphazo*-compound, $COOPh \cdot C_6H_4 \cdot O \cdot PO{:}NPh$ (probably double this), was obtained by heating the oxychlorophosphine with aniline hydrochloride and a little xylene for 12 hours at 180°; it melts at 152°.   C. F. B.

Direct Introduction of Mercury into Aromatic Compounds. By OTTO DIMROTH (*Ber.*, 1898, **31**, 2154—2156. Compare K. A. Hofmann, Abstr., 1898, i, 635).—When benzene is heated for several hours with dry mercuric acetate at 110°, phenylmercuric acetate, $Ph \cdot Hg \cdot OAc$, is formed. Toluene gives an analogous derivative. Phenol and mercuric acetate react in concentrated aqueous solution, when the liquid is warmed; *hydroxyphenyldimercuric acetate*, $OH \cdot C_6H_3(Hg \cdot OAc)_2$, melting at 216—217°, separates out, whilst on treating the mother liquor with sodium chloride, *para-* and *ortho-hydroxyphenylmercuric chlorides*, $OH \cdot C_6H_4 \cdot HgCl$, melting respectively at 219—220° and 152·5°, can be obtained; these form sodium derivatives, and by boiling the sodium derivatives with methylic iodide and alcohol, para- and ortho-anisylmercuric chlorides can, in the last two cases, be obtained. All these compounds are decomposed by hydrochloric acid, the mercury being removed and hydrogen substituted for it; in the case of the phenolic compounds, iodine also removes the mercury and forms iodophenols.   C. F. B.

Derivatives of Anisaldehyde. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1897, [iii], **17**, 510—515).—Claisen has shown that ethylic acetate reacts with benzaldehyde in the presence of sodium, yielding, as chief product, ethylic cinnamate (Abstr., 1890, 891). The author has obtained *ethylic paramethoxycinnamate* by a similar method, the best yield being obtained at a temperature of 15°; as the reaction is

exothermic, the mixture is surrounded by iced water, and after it has been allowed to remain for 12 hours, acetic acid and water are added. The ethylic salt distils between 295° and 320°, and crystallises in brilliant plates melting at 49°. The yield is good if the materials employed are pure ; the ethylic acetate should contain neither alcohol nor water. *Paramethoxycinnamic acid* crystallises from dilute alcohol in long, silky needles melting at 170° (compare Abstr., 1887, 1109). The *dibromide*, $OMe \cdot C_6H_4 \cdot CHBr \cdot CHBr \cdot COOEt$, melts at 114°. *Paramethoxyphenylpropiolic acid*, $OMe \cdot C_6H_4 \cdot C \vdots C \cdot COOH$, obtained when the dibromide is subjected to prolonged treatment with excess of alcoholic potash, is sparingly soluble in water, softens at 132°, and melts and decomposes at 139°. The yield is about 40 per cent. of the theoretical. *Paramethoxyphenylacetylene*, $OMe \cdot C_6H_4 \cdot C \vdots CH$, formed when the preceding acid is heated with excess of aniline until the evolution of carbonic anhydride ceases, boils at 205—212°, forms fairly large crystals melting at 28·5°, and is insoluble in water, but dissolves in alcohol or ether, and yields precipitates with ammoniacal cuprous chloride or silver nitrate. The yield is poor.

Anisyl methyl ketone, $OMe \cdot C_6H_4 \cdot COMe$, formed when paramethoxyphenylpropiolic acid is heated with water at 130°, may be purified by distillation in steam and treatment with light petroleum, when crystals consisting of large plates, and melting at 38·5°, are obtained. A further quantity of the ketone, together with methoxyphenylacetylene, may be separated from the petroleum solution.

Ethylic methylenedioxycinnamate, $CH_2 \underset{O}{\overset{O}{<}} > C_6H_3 \cdot CH \vdots CH \cdot COOEt$,

obtained when ethylic acetate is treated with piperonal in the presence of metallic sodium, melts at 65—68°.   J. J. S.

Action of Chloracetic Chloride on various Aromatic Hydrocarbons in the presence of Aluminium Chloride. By A. COLLET (*Bull. Soc. Chim.*, 1897, [iii], **17**, 506—510).—Chloracetylbenzene (ω-chloracetophenone), $CH_2Cl \cdot COPh$, is readily obtained by Friedel-Craft's method, either at the ordinary temperature or at the boiling point of benzene. When heated again with more benzene and aluminium chloride, it remains unaltered, but when treated with toluene (150 grams to 10 of chloracetophenone) and aluminium chloride (20 grams) at the boiling point of the toluene, it yields *methyldeoxybenzoin*, $COPh \cdot CH_2 \cdot C_6H_4Me$, which may be purified by distillation under diminished pressure and subsequent recrystallisation from boiling alcohol ; it crystallises in small, colourless needles melting at 84—85°.

Chloracetic chloride (50 grams), toluene (200 grams), and aluminium chloride (65—70 grams) react at the ordinary temperature, yielding *parachloracetyltoluene* (p-*tolyl chloromethyl ketone*), $C_6H_4Me \cdot CO \cdot CH_2Cl$, [Me : CO = 1 : 4], which distils at 260—263° and melts at 55·5—56°. When oxidised, it yields terephthalic acid. When heated with an alcoholic solution of potassium acetate, it yields colourless needles of *paratoluoylcarbinol acetate*, $C_6H_4Me \cdot CO \cdot CH_2Ac$, melting at 83—83·5°. Aniline and parachloracetyltoluene, in alcoholic solution, yield *paratolyl anilidomethyl ketone*, $C_6H_4Me \cdot CO \cdot CH_2 \cdot NHPh$, which crystallises

in yellow plates melting at 118—120°.   When parachloracetyltoluene is heated with an excess of toluene and aluminium chloride, it yields *deoxytoluoin* (tolyl methylbenzyl ketone), $C_6H_4Me \cdot CO \cdot CH_2 \cdot C_6H_4Me$, which crystallises in colourless needles melting at 97—98°. A small quantity of the same substance is obtained when chloracetic chloride is boiled with toluene.   *Chloracetylparaxylene* (paraxylyl chloromethyl ketone), $C_6H_3Me_2 \cdot CO \cdot CH_2Cl$ [1:4:2], is obtained when a mixture of paraxylene (25 grams) and chloracetic chloride (27 grams) is added slowly to aluminium chloride (25 grams) covered with a layer of carbon bisulphide ; when recrystallised from alcohol or benzene, it melts at 31—32°, and when oxidised with alkaline permanganate it yields trimellitic acid.

Chloracetylmesitylene(*mesityl chloromethyl ketone*),$C_6H_2Me_3 \cdot CO \cdot CH_2Cl$, obtained in a similar manner, melts at 68·5°, and is sparingly soluble in alcohol ; the yield is good.

Chloracetyldiphenyl, $C_6H_4Ph \cdot CO \cdot CH_2Cl$, is obtained by dissolving diphenyl (10 grams) in an excess of carbon bisulphide, adding aluminium chloride (10 grams) and then gradually chloracetic chloride (8 grams) ; it crystallises from boiling alcohol and melts at 122—123°. When oxidised, it yields paradiphenylcarboxylic acid.   J. J. S.

Coumarin. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1897, [iii], **17**, 515—517).—Salicylaldehyde has been acetylated by Barbier's method (*Compt. rend.*, **90**, 37). The acetyl derivative, $COH \cdot C_6H_4 \cdot OAc$, is readily obtained when the aldehyde (1 mol.) is heated with acetic anhydride (2 mols.) for 6 hours at 180°, but if an excess of the anhydride is employed, namely, double the weight of the aldehyde, coumarin is formed, agreeing in all its properties with coumarin obtained by other methods.   J. J. S.

Action of Organic Acids on Nitriles. By JOHN A. MATHEWS (*J. Amer. Chem. Soc.*, 1898, **20**, 648—668).—When malonic acid is heated with succinonitrile in a sealed tube during 5½ hours at 150°, considerable decomposition occurs, and a small quantity of succinimide is formed, but no malonimide ; when malononitrile is heated with glacial acetic acid, it is almost completely decomposed. On heating cyanacetic acid dissolved in benzene at 190°, it is largely decomposed, although a small quantity of a crystalline *substance* is formed, which melts at 115°, contains nitrogen, and is easily soluble in alcohol, ether, and acetone, but insoluble in benzene ; it appears to consist of *malonimide*, since it is converted into malonic acid when boiled with aqueous potash.

On heating benzoic acid (1 mol.) with succinonitrile (1 mol.), initially during 7 hours at 145°, and subsequently for 5½ hours at 195°, benzonitrile is formed, together with succinimide ; when an excess of benzoic acid (2 mols.) is employed, the same products are formed, a considerable proportion of the acid remaining unacted on. Since no succinic acid was obtained, the author considers that the production of succinimide probably takes place through the intermediate formation of β-cyanopropionic acid, the latter undergoing rearrangement at the temperature employed,

When a mixture of phenylacetic acid and succinonitrile, in molecular proportion, is heated at 150° during 6 hours, phenylacetonitrile is formed, together with a small quantity of phenylacetamide; the latter is probably formed by a small quantity of water present interacting with phenylacetonitrile. When an excess of phenylacetic acid is used (2 mols. to 1 of nitrile), it is not completely acted on under the above conditions; phenylacetonitrile is obtained together with diphenyldiacetamide, the latter being formed by the interaction of benzylic cyanide with the excess of phenylacetic acid.

On heating salicylic acid with acetonitrile during 5 hours at 195—200°, considerable decomposition occurs and small quantities of phenol are formed, although no other product can be isolated.

Anthranilic acid is decomposed when heated with acetonitrile for 5 hours at 220—230°, a product almost completely soluble in water being obtained; the aqueous solution deposits slender *crystals* which melt at 232° and readily sublime, and are converted by boiling concentrated hydrochloric acid into a crystalline *substance* which does not melt at 280°. On heating phthalic acid with propionitrile during $5\frac{1}{2}$ hours at 180—200°, a 92·5 per cent. yield of phthalimide is obtained; the action, however, seems to be complete in $3\frac{1}{2}$ hours. A mixture of phthalic acid and succinonitrile, in molecular proportion, is considerably charred when heated during 5 hours at 220°, phthalimide being formed, together with small quantities of succinimide. Phthalic anhydride does not interact with acetonitrile when heated initially during 4 hours at 145°, and, finally, for $13\frac{1}{2}$ hours at 200—235°; its behaviour, therefore, does not resemble that of acetic anhydride, which easily gives rise to triacetamide under the same conditions. Terephthalic acid is not changed when heated with propionitrile at 260°. On heating homophthalic acid with acetonitrile during 5 hours at 190°, only a small quantity of homophthalimide is obtained, a non-nitrogenous crystalline *substance*, which decomposes and chars at 230° being formed, together with white *crystals* which melt at no definite temperature. Cyanorthotoluic acid, when heated in benzene solution at 190°, is not converted into homophthalimide (compare Gabriel, *Ber.*, 1887, **20**, 2502), but a small quantity of a *substance*, which crystallises in needles and melts at 182°, is formed.

When diphenic acid is heated with acetonitrile during 6 hours at 225—240°, acetic acid is formed, together with a 90 per cent. yield of diphenimide; the latter melts at 217·5°, whilst diphenamide melts at 212—213° when slowly heated, and at 217° when heated rapidly (compare Graebe and Aubin, Abstr., 1889, 145; and Wegerhoff, Abstr., 1888, 1200).

It is usually stated that orthosulphobenzoic acid melts at 250°, whereas it really melts at 68° when containing water of crystallisation, and at 130° when anhydrous; the ammonium hydrogen salt, $COOH \cdot C_6H_4 \cdot SO_3NH_4$, which was originally considered to be the free acid, melts at 250—260°. When orthosulphobenzoic acid (1 mol.) is heated with acetonitrile (1 mol.) for 5 hours at 165—170°, benzoic sulphinide (saccharin) is not formed, but a small quantity of a substance isomeric with it, having no sweet taste; the latter separates

from alcohol in minute crystals, and is possibly the *unsymmetrical sulphobenzimide*, $SO_2 <^{C_6H_4}_{.O.} >C:NH$.

On heating mellitic acid (1 mol.) with acetonitrile (3 mols.) containing a few drops of acetic anhydride during 4 hours at $265-275°$, somewhat impure paramide is obtained; when the mixture is heated initially at $180--200°$ for 3 hours, subsequently at $225-235°$, during the same period, a 90 per cent. yield of paramide is obtained, together with a small quantity of euchroic acid. An attempt to prepare mellitomonimide by heating acetonitrile (1 mol.) with mellitic acid (1 mol.) during $4\frac{1}{2}$ hours at $215-220°$, gave rise to a large quantity of euchroic acid only; a similar attempt, using tetrasodium mellitate, failed, no action taking place at $290°$. Anhydrous euchroic acid is not changed by heating with acetonitrile during $3\frac{1}{2}$ hours at $223°$, but at $240-260°$ it is partially converted into paramide; this reaction indicates that euchroic acid is an ortho-compound. A *para-euchroic acid*, $C_{12}H_4N_2O_8 + 2H_2O$, appears to be formed when disodium mellitate (1 mol.) is heated with acetonitrile (2 mols.) during 5 hours at $225-240°$; it crystallises from water in thin plates, and does not melt or change, except by losing water of crystallisation, when heated at $295°$. It resembles euchroic acid in giving the euchrone test, but differs from it in not yielding paramide when heated with propionitrile during 5 hours at $240-260°$. In making the euchrone test for euchroic acid (compare Schwartz, *Annalen*, 1848, **66**, 46), aluminium amalgam can be used instead of zinc; the action takes place slowly, the aluminium becoming red before the solution shows any colour.

In all the experiments described above, a few drops of acetic anhydride were present to insure anhydrous conditions.   W. A. D.

Action of Aromatic Tetrazochlorides on Methylic and Ethylic Cyanacetates. By G. FAVREL (*Compt. rend.*, 1898, **127**, 116—117. Compare Abstr., 1893, i, 210, 465, 509; 1895, i, 274, and 1896, i, 479).—*Ethylic diphenyldihydrazonecyanacetate*,
$$C_{12}H_8[N_2H:C(CN)\cdot COOEt]_2,$$
produced by adding an alcoholic solution of ethylic cyanacetate to a cold solution of diphenyltetrazochloride and subsequently rendering the mixture alkaline, is a yellow powder melting at $204-206°$, and insoluble in the usual organic solvents, but crystallising from aniline; with alcoholic soda, it yields a disodium derivative. The corresponding *dimethylic* salt melts and decomposes at $270°$.
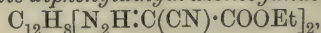
Ethylic diorthotolyldihydrazonecyanacetate is obtained from diazotised tolidine and ethylic cyanacetate, and melts at $224-225°$. The *methylic* salt melts at $270°$.

Ethylic dianisyldihydrazonecyanacetate melts at $283-285°$.

G. T. M.

Action of Tetramethyldiamidobenzhydrol on Para- and Meta-sulphanilic Acids. By SUAIS (*Bull. Soc. Chim.*, 1897, [iii], **17**, 517—519).—Tetramethyldiamidobenzhydrol (54 grams) is dissolved in a solution of sodium parasulphanilate (46·2 grams) and

hydrochloric acid (18 c.c.), in 1 litre of water. The whole is heated at 80—90° during 6 hours, and the products are (1) a yellow, crystalline product which dyes cotton, mordanted with tannic acid, in much the same way as auramines, and is very sensitive to acids. (2) A sulpho-leuco-base which is transformed by lead peroxide into a dye which colours wool green, and is sensitive to alkalis, which decolorise it. (3) Hexamethyltriamidotriphenylmethane. (4) A substance remaining in solution which has not been examined.

A mixture of 34 grams of metasulphanilic acid, 51 grams of the benzhydrol, 530 c.c. of water, and 57 c.c. of hydrochloric acid, when heated on the water bath for from 6 to 12 hours, gives the same products as above, but the yellow substance only forms some 4 per cent. of the total products, the sulpho-leuco-base being the chief constituent. The last compound can be converted into green and blue colouring matters. J. J. S.

Formation of Carbocyclic Compounds from 1 : 5- and 1 : 6-Diketones by Converting them into their Pinacones. By JOHANNES WISLICENUS (*Annalen*, 1898, 302, 191—195. Compare Pusch, Abstr., 1895, i, 666).—The paper introduces the following, which deal with the formation of cyclic compounds on reducing certain diketones. M. O. F.

Dibenzoyldiphenylbutadiene and its Reduction to Tetraphenylbenzene. By JOHANNES WISLICENUS and ADOLF LEHMANN (*Annalen*, 1898, 302, 195—214. Compare Japp and Miller, Trans., 1885, 11).—According as benzil condenses with one or two molecular proportions of acetophenone, 1 : 2-dibenzoylphenylethylene,

$$COPh \cdot CPh{:}CH \cdot COPh,$$
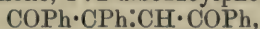
or dibenzoyldiphenylbutadiene, $C_2Ph_2(CH \cdot COPh)_2$, is produced; the former has been already described by Japp and Miller under the name dehydroacetophenonebenzil.

Dibenzoyldiphenylbutadiene, $C_2Ph_2(CH \cdot COPh)_2$, crystallises in yellow needles and melts at 191—192°; the *dioxime* melts and decomposes at 246°. Bromine converts the diketone into a *dibromide* which decomposes at about 170°, and into a tetrabromide. Reduction with zinc dust and glacial acetic acid converts the diketone into a variety of compounds, the separation of which is described in detail in the original paper; the following are the substances in question.

Dibenzoyldiphenylbutane, $C_2H_2Ph_2(CH_2 \cdot COPh)_2$, melts at 243—247°. *Dibenzoyldiphenylbutene*, $COPh \cdot CH{:}CPh \cdot CHPh \cdot CH_2 \cdot COPh$, melts at 220—222°; the *dioxime* crystallises in six-sided plates, and melts at 230°.

Tetraphenyldihydroxydihydrobenzene, $CH{<}^{CPh(OH) \cdot CPh(OH)}_{CPh{-\!-\!-\!-\!-}CPh}{>}CH$,

crystallises from boiling alcohol in colourless, monoclinic prisms, and melts at 170—171°; the *pinacoline*, $C_{30}H_{22}O$, obtained from it by elimination of $1H_2O$, crystallises from boiling alcohol in thin, yellow needles, and melts at 180—181°. *Tetraphenylbenzene*,

$$CH{<}^{CPh{:}CPh}_{CPh \cdot CPh}{>}CH,$$
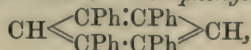
separates from boiling benzene in colourless needles, and melts at 277—278°; Bogdanowska has described an isomeric hydrocarbon which melts at 268—269° (Abstr., 1892, 851). M. O. F.

Ethylic 1 : 2-Dibenzoylglutarate and its Conversion into 1 : 2-Diphenylcyclopentane. By JOHANNES WISLICENUS and CRISTOPH KARL KUHN (*Annalen*, 1898, 215—222).—*Ethylic 1 : 2-dibenzoylglutarate*, $CH_2(CHBz \cdot COOEt)_2$, may be prepared by the action of methylenic iodide on ethylic benzoylacetate under the influence of sodium ethoxide (compare Knoevenagel, Abstr., 1895, i, 48) ; it crystallises from ether in small, lustrous needles, and melts at 130·5°. An alcoholic solution is indifferent towards ferric chloride, but the latter develops a cherry red coloration with the oily modification of the ethereal salt which is associated with the crystals.

1 : 3-*Dibenzoylpropane*, $CH_2(CH_2Bz)_2$, obtained along with γ-benzoylbutyric acid by hydrolysing the oil with 10 per cent. caustic potash, crystallises in nacreous needles and melts at 67·5° ; the *dioxime* forms elongated, lustrous prisms and melts at 62°.

The *pinacone*, $C_{17}H_{18}O_2$, prepared by reducing dibenzoylpropane, is a yellow oil, which, with hydriodic acid and red phosphorus at 150—160°, yields 1 : 2-*diphenylcyclopentane*, $\begin{matrix} CHPh \cdot CH_2 \\ | \\ CHPh \cdot CH_2 \end{matrix}\!\!>\!CH_2$, crystallising from a mixture of ether and alcohol and melting at 108°.

<div align="right">M. O. F.</div>

1 : 3-Dibenzoyl-1 : 3-diphenylpropane and its Reduction to Tetraphenylcyclopentane. By JOHANNES WISLICENUS and HAROLD CARPENTER (*Annalen*, 1898, 302, 223—236).—1 : 3-*Dibenzoyl-1 : 3-diphenylpropane*, $CH_2(CHPh \cdot COPh)_2$, prepared by the action of formaldehyde on deoxybenzoin under the influence of caustic potash, melts at 145·5—146·5° ; it is structurally isomeric with deoxybenzoinbenzylideneacetophenone which melts at 189° (Abstr., 1895, i, 48).

1 : 2 : 3 : 5-*Tetraphenylcylopentane-1 : 2-diol*, $\begin{matrix} OH \cdot CPh \cdot CHPh \\ | \\ OH \cdot CPh \cdot CHPh \end{matrix}\!\!>\!CH_2$, the pinacone obtained by reducing dibenzoyldiphenylpropane, occurs in two forms, according as an acidic or alkaline reducing agent is employed. When prepared by means of zinc dust and glacial acetic acid, it crystallises from alcohol in needles and melts at 138° ; the modification obtained through the agency of sodium amalgam, however, crystallises in colourless, lustrous needles and melts at 239—240°.

Tetraphenylcyclopentane, $\begin{matrix} CHPh \cdot CHPh \\ | \\ CHPh \cdot CHPh \end{matrix}\!\!>\!CH_2$, prepared by reducing the pinacones with hydriodic acid and red phosphorus at 140—150°, crystallises from alcohol in colourless lustrous needles, and melts at 80·5—81°.

Tetraphenylcyclopentadiene, $\begin{matrix} CPh \colon CPh \\ | \\ CPh \colon CPh \end{matrix}\!\!>\!CH_2$, arises from the action of oxalic acid at 138° on the pinacone first described ; it crystallises from a mixture of alcohol and benzene, and melts at 177°. The *dibromide*, $C_{29}H_{20}Br_2$, crystallises from alcohol in small, red plates and melts at 151·5—152°.

2 : 3 : 5 : 6-*Tetraphenylpyridine*, $CH\!<\!\!\begin{matrix} CPh \cdot CPh \\ CPh \colon CPh \end{matrix}\!\!>\!N$, is prepared by heating 1 : 3-dibenzoyl-1 : 3-diphenylpropane with alcoholic hydroxyl-

amine hydrochloride at 150°; it melts at 233·5°, that is to say, 54·5° higher than 2 : 4 : 5 : 6-tetraphenylpyridine (Knoevenagel, *loc. cit.*).

M. O. F.

Derivatives of Benzylidenediacetophenone: 1 : 2 : 4-tri-phenylcyclopentane. By JOHANNES WISLICENUS and FRANK H. NEWMAN (*Annalen*, 1898, **302**, 236—244).—1 : 2 : 4-*Triphenylcyclopentane*-1 : 2-*diol*, $\begin{matrix} \text{OH·CPh·CH}_2 \\ | \\ \text{OH·CPh·CH}_2 \end{matrix}$>CHPh, is the pinacone prepared by reducing benzylidenediacetophenone (Abstr., 1896, i, 556) with zinc dust and acetic acid; it crystallises from light petroleum and melts at 142°.

1 : 2 : 4-*Triphenylcyclopentadiene*, $\begin{matrix} \text{CPh:CH} \\ | \\ \text{CPh:CH} \end{matrix}$>CHPh, formed by the action of concentrated hydrochloric acid on the pinacone dissolved in alcohol, crystallises in yellowish needles and melts at 149°. The *dibromide*, $C_{28}H_{16}Br_2$, melts at 157°.

1 : 2 : 4-*Triphenylcyclopentane*, $\begin{matrix} \text{CHPh·CH}_2 \\ | \\ \text{CHPh·CH}_2 \end{matrix}$>CHPh, prepared by heating the unsaturated hydrocarbon with hydriodic acid at 160—170°, is a pale yellow oil, and boils at 285° under a pressure of 50 mm.

1 : 3 : 6-*Triphenylpyridine*, CPh$\begin{matrix} \text{CH·CPh} \\ \diagup \quad \diagdown \\ \text{CH:CPh} \end{matrix}$N, produced by the action of hydroxylamine hydrochloride in a reflux apparatus, crystallises from alcohol in colourless prisms, and melts at 137·5°. Free hydroxylamine, on the other hand, converts benzylidenediacetophenone into the *oxime* and the *dioxime* which melt at 144° and 163·5° respectively.

M. O. F.

New Reaction for Paraquinones and Paraquinoidal Compounds. By RICHARD MÖHLAU (*Ber.*, 1898, **31**, 2351—2352).—Benzhydrol and its derivatives combine with paraquinones and similarly constituted compounds, the condensation being accompanied by elimination of water. Benzoquinone and benzhydrol give rise to *benzoquinonebidiphenylmethane*, $C_6H_2O_2(CHPh_2)_2$, which crystallises in yellow prisms and melts at 238°.

If one of the hydrogen atoms adjacent to a quinone oxygen atom is already substituted, then only one hydrol residue enters the quinone molecule. In this manner, *a-naphthaquinonediphenylmethane*, $C_{10}H_5O_2·CHPh_2$, results from the action of benzhydrol on a-naphthaquinone; it crystallises in yellow prisms and melts at 185°.

a-Naphthaquinonetetramethyldiamidodiphenylmethane,

$$C_{10}H_5O_2·CH(C_6H_4·NMe_2)_2,$$

is produced from a-naphthaquinone and tetramethyldiamidodiphenyl-carbinol; it forms dark red leaflets melting at 167°.

Paranitrosophenoltetramethyldiamidodiphenylmethane,

$$NOH:C_6H_3O·CH(C_6H_4·NMe_2)_2,$$

produced from tetramethyldiamidodiphenylcarbinol and paranitroso-phenol, forms dark yellow prisms and melts at 217°.

Paranitrosodimethylanilinetetramethyldiamidodiphenylmethane,

$$O\begin{matrix} \text{——N} \\ \diagup \quad \diagdown \\ \text{NMe}_2 \end{matrix}C_6H_3·CH(C_6H_4·NMe_2)_2,$$
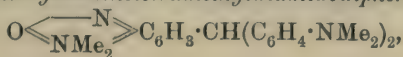
the analogous compound from nitrosodimethylaniline, crystallises in yellow prisms and melts at 212°.

Paraquinonoid dyes form similar condensation products.

A blue colouring matter obtained from Meldola's blue and the above diamidohydrol is described in the D.R.-P. No. 68381.

These condensation products behave as leuco-bases of the triphenylmethane series, and on oxidation yield colouring matters which contain two chromphoric groups.

A blue *colouring matter* having the constitution

$$NMe_2Cl:C_6H_4:C(C_{10}H_5O_2)\cdot C_6H_4\cdot NMe_2,$$
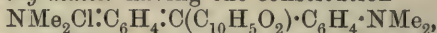
is obtained by oxidising α-naphthaquinonetetramethyldiamidodiphenylmethane with lead peroxide.　　　　　　　　　　　　G. T. M.

Constitution of the Dinitro-derivative obtained by the Nitration of β-Naphthol. By FRIEDRICH KEHRMANN and M. MATIS (*Ber.*, 1898, **31**, 2418—2419).—The nitro-compound obtained by the nitration of β-naphthol can also be prepared from dinitro-β-naphthylamine. The last compound can readily be converted into a dinitronaphthalene, which, on reduction, yields a diamido-derivative, and this is converted by Sandmeyer's reaction into 1 : 3′-dichloronaphthalene. The *diamido*-compound is, therefore, 1 : 3′-diamidonaphthalene, and the original dinitro-β-naphthylamine has the constitution [$(NO_2)_2 : NH_2 = 1 : 3′ : 2$], since it is already known that the two groups in the same ring are in the ortho-position (Loewe, Abstr., 1891, 1424). Hence dinitro-β-naphthol has the constitution [$OH : (NO_2)_2 = 2 : 1 : 3′$].
　　　　　　　　　　　　　　　　　　　　　　　　　　A. H.

Naphthopicric Acid. By FRIEDRICH KEHRMANN and WANDA HABERKANT (*Ber.*, 1898, **31**, 2420—2424).—The commercial product prepared by the nitration of " Martius' yellow " contains, in addition to naphthopicric acid, a trinitronaphthol which melts at 145°, and is converted by oxidation into 1 : 2 : 4-nitrophthalic acid, and therefore has the constitution [$OH : (NO_2)_3 = 1 : 2 : 4 : 2′$ or $3′$], the exact position of one nitro-group not having been as yet ascertained. Naphthopicric acid is converted by reduction into diamidonaphthaquinonimide, as previously described by Diehl and Merz (Abstr., 1878, 250). When this substance is boiled with water, it is converted into a mixture of 1′-*amido*-2-*hydroxy*-1 : 4-*naphthaquinone* and 2 : 1′-diamido-1 : 4-naphthaquinone. The former of these crystallises in dark brown plates melting at 221°, and forms a blood-red solution in alkalis, whilst the *diacetyl* derivative crystallises in orange-yellow granules ; 2 : 1′-*diamido*-1 : 4-*naphthaquinone*, on the other hand, is insoluble in alkalis, and crystallises in dark red tablets which decompose above 200°. No hydroxynaphthaquinonimide derivative could be obtained. The trinitronaphthol melting at 145° is converted by reduction into a *triamidonaphthol*, the hydrochloride of which crystallises in long, colourless needles ; this salt readily oxidises in the presence of free acid, and is converted by ferric chloride into 2 : 3′-*diamido*-1 : 4-*naphthaquinonimide*, which crystallises in orange-red needles. The *hydrochloride*, $C_{10}H_{14}N_3OCl_3 + H_2O$, is readily soluble in water, and forms dark brown needles, whilst the *platinochloride* crystallises in very sparingly soluble, almost black, needles.　　A. H.

Chromotropic Acid. By Ludwig Hantower and Ernst Täuber (*Ber.*, 1898, **31**, 2156—2159).—Phenylazochromotropic acid (chromotropic acid = $C_{10}H_4(OH)_2(SO_3H)_2$ [$= 1 : 1' : 3 : 3'$]), which the dye-works' chemists regard as a 2-azo-compound, is that in reality, for when it is reduced with stannous chloride, it yields an amidochromotropic acid that must be a 2-amido-compound, because oxidation with cooled concentrated nitric acid converts it into an acid that is characterised by its reaction with orthotolylenediamine (it forms a *tolylhydroxynaphthazinedisulphonic acid*) as 1'*-hydroxy-*1 : 2*-naphthaquinone-*3 : 3'*-disulphonic acid.* The *sodium* salts of these two acids were prepared ; they are respectively brown and golden-yellow in colour. C. F. B.

Ethereal Oils. By Schimmel and Co. (*Chem. Centr.*, 1898, i, 258—259; from Schimmel and Co.'s *Bericht*, 1897, October).—Malabar cardamoms oil, prepared from *Elettaria cardamomum Matton*, which yields 2·14 per cent., is soluble in 4 parts of 70 per cent. alcohol, has a sp. gr. = 0·943 at 15°, a rotatory power at 19° = + 34° 52' (100 mm. tube), and a saponification number = 132. The oil contains cineol, a solid terpineol of rotatory power = + 83° 31' at 21°, and considerable quantities of alkylic acetates. Siam cardamoms oil is a semi-solid oil, obtained from *Ammomum cardamomum L.*, which yields 2·4 per cent., is soluble in 1·2 parts of 80 per cent. alcohol, has a sp. gr. = 0·905 at 42°, a rotatory power at 42° = + 38° 4', and a saponification number = 18·8. The acetyl derivative has a saponification number = 77·2. The oil contains dextroborneol and dextrocamphor. Cameroon cardamoms oil, prepared from *Ammomum angustifolium Sonnerat*, which yields 2·33 per cent., is soluble in 7—8 parts of 80 per cent. alcohol, has a sp. gr. = 0·907 at 15°, and a rotatory power = − 20° 34'. It contains large quantities of cineol, and cannot be used as a substitute for Ceylon cardamoms oil. Oil of grains of Paradise, obtained from *Ammomum Melegueta Roscoe*, which yields 0·75 per cent., is soluble in 10—11 parts of 90 per cent. alcohol, has a sp. gr. = 0·894 at 15°, and a rotatory power = + 3° 58'.

Fir oil, obtained from the needles of *Pinus sylvestris L.*, dissolves in 8 parts of 90 per cent. alcohol with faint opalescence, has a sp. gr. = 0·884 at 15°, a rotatory power at 18° = − 24° 8', and a saponification number = 34·8, which corresponds with a content of 12·1 per cent. of bornylic acetate. Hemlock oil, from the needles of *Abies canadensis L.*, is soluble in equal parts of 90 per cent. alcohol, has a sp. gr. = 0·911 at 15°, a rotatory power = − 25° 22' at 16°, and contains 38 per cent. of bornylic acetate. Spruce oil, from the needles of *Picea nigra L.* (or *alba?*), is soluble in half its volume of 90 per cent. alcohol, has a sp. gr. = 0·913 at 15°, a rotatory power = − 23° 50' at 18°, and contains 38·1 per cent. of bornylic acetate. The two preceding oils, which both contain lævorotatory pinene and lævorotatory bornylic acid, cannot be distinguished from each other.

Dalmatian oil of rosemary is obtained by distilling the leaves, which yield 1·4—1·75 per cent., has a sp. gr. = 0·904—0·913 at 15°, a rotatory power varying from + 4° 16' to 8° 52', and contains pinene and camphene. Two samples of the oil contained 5—6 per cent. of bornylic acetate and 17—19 per cent. of borneol. Oil of rosemary

should be dextrorotatory, have a sp. gr. greater than 0·9 at 15°, and dissolve in half a part of 90 per cent. alcohol, or in 10 parts of 80 per cent. alcohol. When one-tenth of its volume is distilled off, the distillate should be dextrorotatory.

The following new oils, obtained by distilling the plants, are also described. Oil of pepperwort, prepared from flowering *Satureja hortensis*, which yields 0·097 per cent., is soluble in 9 parts of 80 per cent. alcohol, has a sp. gr. = 0·904 at 15°, a rotatory power = + 0° 4', and contains 38 per cent. of carvacrol. The oil from *Satureja montana*, which yields 0·18 per cent., is soluble in 4·5 parts of 70 per cent. alcohol, has a sp. gr. = 0·939 at 15°, a rotatory power = – 2° 35', and contains 65 per cent. of phenols which consist principally of carvacrol. Xanthorrhœa resin oil, from the yellow Australian resin of *Xanthorrhœa hastilis R. Br.*, which yields 0·37 per cent., has an odour like storax, a sp. gr. = 0·937 at 15°, a rotatory power = – 3° 14', a saponification number = 74·3, an acid number = 4·9, an etherification number = 69·4, and contains styrene. The saponified oil boils at 145—240° (compare Hildebrand, *Arch. Pharm.*, **234**, 698). Balsam oil is prepared from the flowering plant of *Tanacetum balsamita L.*, which yields 0·064 per cent., has an odour of tansy, a sp. gr. = 0·943 at 15°, a rotatory power = – 53° 48' at 16°, and boils at 207—283° Larch oil, from the needles of *Larix europœa D.C.*, which yields 0·22 per cent., is soluble in 5 parts of 90 per cent. alcohol, has a sp. gr. = 0·878 at 15°, a rotatory power = + 0° 22' at 18°, a content of alkylic salt corresponding with 8·1 per cent. of bornylic acetate, and a content of alcohol corresponding with 6·14 per cent. of borneol ; 70 per cent. of the oil distils at 160—180°.

When terpineol is heated with sodium acetate and acetic anhydride for 45 minutes, 84 per cent. of terpenylic acetate is obtained ; by prolonging the action for 2 hours, the yield is reduced to 78 per cent. In reply to Erdmann and Huth (*J. pr. Chem.*, 1897, [ii], **56**, 1), the authors would abolish the term rhodinol, which is used both for citronellol and for a mixture of citronellol and geraniol, and they state also that geraniol free from chlorine can be obtained by preparing the calcium chloride compound and shaking the oil liberated from it with warm water. The suggestion that the firm's commercial geraniol contains either chlorine compounds of higher boiling points and disagreeable odour or citronellol is also repudiated.   E. W. W.

Ethereal Oil of Angostura Bark. By HEINRICH BECKURTS and JULIUS TROEGER (*Arch. Pharm.*, 1898, **236**, 392—408. Compare Abstr., 1898, i, **37**, 202).—The authors have endeavoured, without success, to again isolate the substance previously called by them "galipen alcohol." The amount of alcohol in the raw oil is, as shown by the acetyl value, about 14 per cent.

The right-handed terpene "galipene" (rotation in 100 mm. tube = + 18°, and not [α]$_D$ = + 18° as previously stated) is not originally present in the oil, but is probably a product of inversion.

The left-handed sesquiterpene was extracted from the hydrobromic acid additive product of the raw oil on treatment with aniline, and, although it could not be obtained in a pure state, appears to

be cadinene. This conclusion was arrived at from the consideration of its physical constants, and the properties of its hydrochloride, hydrobromide, and hydriodide.

The inactive sesquiterpene (b. p. 255—260°), isolated previously from an inactive portion of the oil, shows some resemblance to caryophyllene, and the authors propose to call it " galipene," a name which they formerly gave to the right-handed terpene. With hydrobromic acid, it gives an oily, unstable additive product.

Acetic anhydride has no inverting action on either cadinene or the inactive terpene, and, therefore, the formation of the right-handed terpene is not due to this cause. The raw, left-handed oil is, however, inverted by simple distillation, and hydrobromic acid seems to convert the right-handed terpene into the left-handed cadinene. A. W. C.

Acids in Essence of Geranium. By JULIAN FLATAU and H. LABBÉ (*Compt. rend.*, 1898, **126**, 1876—1879).—Indian essence of geranium contains no free acid, but when boiled with alcoholic potash it yields geraniol and an acid, $C_{14}H_{28}O_2$, which melts at 28·2°, and seems to be an isomeride of myristic acid. The silver, barium, calcium, and cupric salts were analysed; the first melts and decomposes at 191—192°, and the last contains $1H_2O$, and melts at 74—75°. The Indian essence also contains small quantities of acetic and butyric acids.

Bourbon essence of geranium contains some free acid, and when treated with alcoholic potash yields an acid, $C_{10}H_{18}O_2$, the silver salt of which melts and decomposes at 158°. The Bourbon essence also contains some acetic acid and a small quantity of valeric acid.

C. H. B.

"Oil of Petit Grain." By JACQUES PASSY (*Bull. Soc. Chim.*, 1897, [iii], **17**, 519. Compare Semmler and Tiemann, Abstr., 1892, 868).— In addition to the substances isolated by Semmler and Tiemann, the author also has found geraniol in oil of petit grain. J. J. S.

Terpenes and Ethereal Oils. Fenchone. By OTTO WALLACH [and M. HERTZ] (*Annalen*, 1898, **302**, 371—387. Compare Abstr., 1898, i, 486).—When lævorotatory fenchylic alcohol, prepared by reducing *d*-fenchone, is treated with phosphorus pentachloride, and hydrogen chloride removed from the product by the action of bases, the hydrocarbon fenchene, $C_{10}H_{16}$, is obtained. It has been hitherto supposed that this terpene is an individual substance, but finding that certain specimens on oxidation yielded hydroxyfenchenic acid melting at 138—139°, instead of at 152—153° (compare *loc. cit.*), the author has submitted the matter to investigation. As a result, it appears that fenchylic alcohol gives rise to two fenchylic chlorides, and these to two fenchenes, one dextrorotatory, and the other lævorotatory; as both are derived from dextrorotatory fenchone, the author distinguishes them as *Dd*-fenchene and *Dl*-fenchene, respectively.

The rotation of fenchylic chloride, prepared from *Dl*-fenchylic alcohol, has been observed to vary between the limits $a_D = -13°$ and $a_D = +5·1°$, in a 1-decimetre tube; the direct product is lævorotatory, but the subsequent treatment modifies the rotatory power to a degree which has not been exactly determined. Strongly lævorotatory fen-

chylic chloride gives rise to *l*-fenchene ; feebly lævorotatory, or nearly inactive chloride, however, yields *d*-fenchene, the observed limits of rotation for these two hydrocarbons being $a_D = \pm 21°$ in a 1-decimetre tube. In order to obtain *d*-fenchene, it is necessary to employ fenchylic chloride which has not been distilled, and *l*-fenchene is prepared by heating *d*-fenchene with alcoholic sulphuric acid during several hours, and may be also obtained by fractional oxidation with potassium permanganate. Whilst *Dl*-fenchene is attacked but slowly by a 3 per cent. solution of potassium permanganate, yielding the hydroxy-fenchenic acid already described (*loc. cit.*, 488), *Dd*-fenchene is oxidised in a few minutes.

Dl-Hydroxyfenchenic ·acid crystallises from dilute acetone in leaflets melting at 152—153°; it has the specific rotatory power $[a]_D = -56·8°$.

Dd-Hydroxyfenchenic acid crystallises from dilute acetone in well-formed, transparent prisms and melts at 138—139°; it has the specific rotatory power $[a]_D = +7·69°$.

Ld-Hydroxyfenchenic acid, prepared from *l*-fenchone, melts at 152—153°, and has the specific rotatory power $[a]_D = +57·3°$; the *racemic hydroxyfenchenic acid* melts at 142—143°.

Fenchylic chloride is slowly oxidised by potassium permanganate, yielding *Dl*-hydroxyfenchenic acid, and is produced when hydrogen chloride is passed into a solution of fenchene in glacial acetic acid.

Dd-Fenchocamphorone, obtained by oxidising *Dl*-hydroxyfenchenic acid (*loc. cit.*), melts at 109—110°, and has $[a]_D = +14·64°$; the oxime has $[a]_D = -50·30°$, and the *semicarbazone*, which melts and effervesces at 210—212°, has $[a]_D = -131·3°$.

Dl-Fenchocamphorone, obtained by oxidising *Dd*-hydroxyfenchenic acid, melts at 62—63°, and boils at 201—202°; it is very volatile, and has $[a]_D = -16·69°$. The *oxime* melts at 54—56°, and has $[a]_D = +49·03°$, whilst the *semicarbazone*, which crystallises in prisms melting at 204—206°, has $[a]_D = +58·11°$.

From these results, the author draws the important conclusion that an ethylenic linkage, occurring in two stereoisomeric substances, does not in each case exhibit the same degree of stability towards potassium permanganate.   M. O. F.

Lemon-grass Oil. By W. STIEHL (*J. pr. Chem.*, 1898, **58**, 51—101).—By carefully distilling 50 kilos. of lemon-grass oil with steam, and collecting the distillate in separate fractions, cymene, α-limonene, and dipentene were detected, but neither geraniol nor citronellal. The bulk of the oil consisted of a mixture of aldehydes, which it was not found possible to separate satisfactorily by distillation under diminished pressure. The following method, or modifications of it, was consequently adopted. The mixture of aldehydes of lemon-grass oil (1 part) is shaken with a 35 per cent. solution of sodium hydrogen sulphite (2 parts) and water (2 parts) until the crystals that form at first have disappeared. Allolemonal (*l*-licarhodal, Barbier and Bouveault, Abstr., 1896, i, 311, 345) is then present as an oil, and is removed ; the aqueous solution yields no aldehydes when treated with sodium carbonate in the cold, but when it is shaken with strong caustic soda, citriodoraldehyde (Dodge, Abstr., 1891, 285)

separates as an oil. If, however, when the mixture of aldehydes is shaken with the sulphite solution, precautions are taken to keep the temperature low until the crystalline compound has been formed, after which the temperature is allowed to rise to about 45—50°, and the mixture is then left in a cool place for 24 hours, crystals are obtained which yield geranial (or citral: Semmler, Abstr., 1891, 539) when they are freed from oil and decomposed with sodium carbonate solution at 45°. The method of separation depends on the fact that all three aldehydes form compounds of the usual type with sodium hydrogen sulphite in the cold; this reaction is attended with the development of heat, and the consequent rise of temperature, if it be not prevented, effects the decomposition of the allolemonal compound (which takes place at about 60° in aqueous solution) and converts the citriodoraldehyde compound into a compound with 2 mols. of sodium hydrogen sulphite (decomposed by aqueous sodium carbonate only on heating, although by caustic soda in the cold), and the geranial compound into a true sulphonate (which is not decomposed, even by caustic soda). This behaviour of citriodoraldehyde resembles that of cinnamaldehyde (Heusler, Abstr., 1891, 1052); hence the former also may be assumed to contain the grouping ·CH:CH·CHO. The semicarbazones (Thiele and Stange, Abstr., 1894, i, 165) and β-naphthocinchonic acid derivatives (Doebner, Abstr., 1895, i, 261) of these three aldehydes were prepared; except in the case of allolemonal, the crude semicarbazones could be separated by fractional crystallisation from methylic alcohol into two modifications; these were not obtained pure in the case of citriodoraldehyde semicarbazone. The aldehydes, C_9H_{15}·CHO, were mixed at 0° with excess of acetone, alcoholic sodium ethoxide was added gradually, and, after a short interval, aqueous tartaric acid; in this way, ketones,

$$C_9H_{15}·CH:CH·CMeO,$$
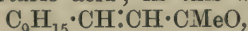
were obtained, respectively citriodorylidene-acetone, allolemonylidene-acetone, and geranylidene-acetone; of these, the last is identical with Tiemann's pseudoionone, whilst the first two correspond respectively to his hypothetical violet-ketones, II and I (*Ber.*, 1898, 31, 811, 853); the semicarbazone of each was prepared. The properties of these compounds are tabulated at the end of the abstract. For the aldehydes themselves, the following formulæ are adopted: citriodoraldehyde, CMe_2:CH·CH_2·CH_2·CMe:CH·CHO; allolemonal, CMe_2:CH·CH:CH·CHMe·CH_2·CHO; geranial,

$$CMe_2:CH·CH_2·CH:CMe·CH_2·CHO.$$
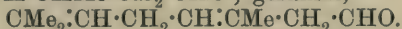
The proportions of the substances found in a genuine sample of lemon-grass oil were: hydrocarbons, 12—50; citriodoraldehyde, 40—50; allolemonal, 25—30; geranial, 8—10 per cent. Probably, the geranial was formed by the action of the sodium hydrogen sulphite, and does not exist in the original oil at all; if the oil is treated with acid agents, a large yield of geranial (citral) is obtained, for the citriodoraldehyde and allolemonal are converted by acids, more or less completely, into geranial.

It follows from the composition of lemon-grass oil thus ascertained that the "artificial oil of violets" prepared from it cannot be identical (compare Doebner, Abstr., 1898, i, 676) with the ionone pre-

pared by Tiemann's method from citral (geranial); it must be a mixture of this substance with Tiemann's two hypothetical "violet-ketones." Nor can calcium hydroxide act as the condensing agent in its formation, for the three aldehydes in question, as also their compounds with acetone, are decomposed by alkalis.

	Citriodor-aldehyde.	Allolemonal (*l*-licarhodal).	Geranial (citral).
Boiling point under 12 mm.	108—109°	117·5—119°	111—112°
,, ,, 760 ,,	228—229°	233—235°	225—227°
Sp. gr. at 20°	0·8883	0·9017	0·8868
Index of refraction n_D at 20°........	1·48538	1·48316	1·48752
Rotation a_D per 1 dm.	$\pm 0°$	$- 5° 6'$	$\pm 0°$
Melting point of semicarbazone ...	134°	169°	141°
,, *a*-semicarbazone...	?	—	160° (plates)
,, *β*- ,,	?	—	150° (needles)
,, naphthocinchonic compound...........................	204°	235°	197°

Products of Condensation with Acetone.

Boiling point under 12 mm..........	149—152°	157—159°	143—145°
Sp. gr. at 20°	0·8980	0·9000	0·9037
Index of refraction n_D at 20°........	1·52903	1·53150	1·52736
Melting point of semicarbazone ...	110—112°	142—143°	134—135°

C. F. B.

Conversion of Linalool into Terpineol Melting at 35°. By KARL STEPHAN (*J. pr. Chem.*, 1898, [ii], **58**, 109—120).—Barbier's licarhodol (Abstr., 1893, i, 544) was prepared by heating *l*-linalool with acetic anhydride for 8 hours (5 would suffice) at 150—160°, and shown to be a mixture of about 85 parts of geraniol with 15 of *d*-terpineol. The presence of geraniol has been admitted already; as regards terpineol, after 26 fractionations a fraction was obtained from which it crystallised out in a freezing mixture.

When linalool is heated with acetic acid, some *d*-terpineol is formed also. In the cold, acetic acid has practically no action, but if to the solution of linalool in three times its weight of acetic acid $\frac{1}{2}$ per cent. of sulphuric acid be added and the temperature kept below 20°, about 45 per cent. is converted into *d*-terpineol and 10 into geraniol; in light petroleum, instead of acetic acid, solution, the sulphuric acid has no such action. Formic acid acts violently on *l*-linalool, forming dipentene and terpinene; if, however, the temperature is kept below 20°, 50 per cent. of the linalool is converted into *d*-terpineol. In a similar fashion, formic acid converts *d*-linalool (coriandrol) into *l*-terpineol.   C. F. B.

Bromocamphor. By CHARLES MOUREU (*Bull. Soc. Chim.*, 1897, [iii], **17**, 552—553).—The author has obtained a considerable amount of phosphorus tribromide by heating equivalent quantities of bromo-camphor and of phosphoric anhydride at about 200°.   J. J. S.

Camphoronic Acid. By OSSIAN ASCHAN (*Annalen*, 1898, **302**, 51—76. Compare Bredt, Abstr., 1898, i, 263).—Three structurally different anhydrocamphoronic acids are theoretically possible. The author describes experiments carried out with a view to ascertaining whether

more than one member of this group exists, but although the question cannot be regarded as finally settled, he considers that camphoronic acid yields the same anhydride by the following methods : 1, distillation ; 2, heating at 105° ; 3, heating at 200° ; 4, action of acetic chloride on the dry acid at common temperatures ; 5, action of acetic chloride on the acid suspended in boiling ether.

Methylic dihydrogen camphoronate, prepared by the action of sodium methoxide (2 mols.) on anhydrocamphoronic acid, and treatment of the product with sulphuric acid, crystallises from a small quantity of water in lustrous, flattened prisms or long needles ; when plunged into a bath at 120°, it melts at 141—142°, but is identical with the compound described by Bredt (Abstr., 1895, i, 242). The difference in melting point arises from the manner in which the two specimens were heated.

Two methylic anhydrocamphoronates have been described by Bredt (Abstr., 1895, i, 242), and although the salts are not interconvertible by the action of heat, both are produced when methylic iodide acts on sodium or silver anhydrocamphoronate. The *sodium* salt of anhydrocamphoronic acid is a lustrous, crystalline substance, and the *silver* salt forms microscopic leaflets ; the sodium salt, when heated with methylic iodide at 135—140°, and the silver salt on the waterbath, are both of them converted into a mixture of α- and β-methylic anhydrocamphoronates. In order to explain this fact, it is necessary to suppose that the anhydride ring in anhydrocamphoronic acid is labile, and, undergoing rearrangement, yields a second ethereal salt, structurally isomeric with the first.

The author regards anhydrocamphoronic acid and the α-methylic salt as having a constitution represented by the formulæ

$$\begin{matrix} CMe_2 \cdot CO \\ | \qquad \qquad >O \\ COOH \cdot CH_2 \cdot CMe{-}CO \end{matrix} \quad and \quad \begin{matrix} CMe_2 \cdot CO \\ | \qquad \qquad >O \\ COOMe \cdot CH_2 \cdot CMe{-}CO \end{matrix}$$

respectively. M. O. F.
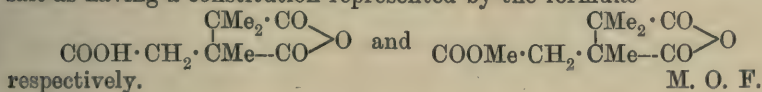
Olibanum. By ALEXANDER TSCHIRCH and HALBEY (*Arch. Pharm.*, 1898, **236**, 487—503).—"*Olibanum electum*" is extracted with 90 per cent. alcohol, and the concentrated extract poured into water acidified with hydrochloric acid, when a clear, yellow resin is precipitated, and a bitter principle goes into solution. By repeating this process and distilling the residue with steam to get rid of an ethereal oil, the pure resin is obtained as a clear, yellow mass easily soluble in the ordinary organic solvents. When dissolved in ether and extracted with caustic soda, *boswellic acid*, $C_{32}H_{52}O_4$, is obtained as a white powder melting at 150°, and showing little tendency to crystallise. It can neither be acetylated nor benzoylated. The *sodium, potassium, barium*, and *copper* salts are described. The resin probably contains some boswellic acid in the form of an ethereal salt, and also *olibano-resen*, $(C_{14}H_{22}O)_n$, a powder insoluble in sodium hydroxide and melting at 62°.

The portion of olibanum insoluble in alcohol consists principally of a gum containing magnesium, calcium, and arabic acid.

A tabulated list of the constituents of some drugs is given, and also of the behaviour of a large number of resinous substances towards the cholesterol reaction. A. W. C.

Action of Nitric Acid on Ouabain. By ALBERT ARNAUD (*Compt. rend.*, 1898, **126**, 1873—1876).—When ouabain is treated with nitric acid of sp. gr. = 1·2, it is only partially oxidised, and no oxalic acid is formed, but hydrolysis takes place, and insoluble nitro-derivatives are produced. If a mixture of 100 grams of ouabain and 300 c.c. of the acid is heated to about 40° until the reaction begins, and the temperature developed is not allowed to exceed 75°, a nitro-derivative, $C_{23}H_{24}(NO_2)_2O_6$, is formed, and crystallises from acetone in yellowish, silky needles which melt and decompose at about 300°. It behaves as a dibasic acid; the potassium and sodium salts are crystallisable, and form intense orange-red, aqueous solutions; the calcium salt is similar, but less soluble; the ammonium salt forms golden-yellow needles.

If the action of the acid takes place at a temperature not exceeding 15°, a small quantity of another nitro-derivative, $C_{23}H_{25}(NO_2)O_6$, is obtained as well as the preceding compound. It is almost insoluble in all neutral solvents, but dissolves readily in alkalis, forming intense orange solutions, from which it is reprecipitated on the addition of excess of acid. It melts and decomposes at about 280°. The ammonium salt, $C_{23}H_{24}(NO_2)O_6,NH_4$, forms small, yellow prisms almost insoluble in water; the other salts are orange or orange-red.

Both nitro-derivatives are derived from the compound $C_{24}H_{36}O_8$, which results from the hydrolysis of ouabain, and which, in presence of nitric acid, is both oxidised and nitrated.   C. H. B.

Digitoxin and Digitalin. By HEINRICH KILIANI (*Ber.*, 1898, **31**, 2454—2464).—Digitoxigenin has a molecular weight in naphthalene, as determined by Baumann-Fromm's method, of 405—412; the formula $C_{22}H_{32}O_4$ requires 360.

Digitoxoseoxime, $C_6H_{13}NO_4$, obtained by treating digitoxose with hydroxylamine, crystallises in concentrically arranged groups of shining needles, is excessively soluble in water and alcohol, and melts at 102°; it no longer exhibits the blue coloration so characteristic of digitoxose on addition of ferric chloride. The air-dried crystals of the oxime change after several months to a yellow, gum-like mass. The *lactone* of digitoxosecarboxylic acid, $C_7H_{12}O_5$, made by mixing digitoxose with concentrated hydrocyanic acid and ammonia, is purified by preparing the barium salt of the acid, and is crystallised from 50 per cent. alcohol; it melts at 153—154°; *calcium digitoxose-carboxylate*, $(C_7H_{13}O_6)_2Ca$, prepared by boiling an aqueous solution of the pure lactone with calcium carbonate, contains 9·15 per cent. of calcium, a number which materially assists in the exclusion of the formula $C_9H_{18}O_6$ for digitoxose.

The colour reactions of digitoxose, which are not exhibited by arabinose, rhamnose, dextrose, galactose, levulose, or sorbose, add probability to the view, already expressed by the author, that digitoxose is a cyclic compound, and in that case its formula, $C_6H_{12}O_4$, would indicate that a true carboxyl group is not present, but that two hydroxyl groups are attached to one carbon atom.

Analyses of digitoxin, and estimations of the digitoxigenin formed from it by hydrolysis, gave results which are in agreement with the

formula $C_{34}H_{54}O_{11}(=C_{22}H_{32}O_4+2C_6H_{12}O_4-H_2O)$. Attempts to determine its molecular weight in acetic acid were found to be valueless, owing to the unavoidable decomposition of the substance.

Anhydrodigitoxigenin, $C_{22}H_{30}O_3$, is made by shaking digitoxigenin with five parts each of 95 per cent. alcohol and concentrated hydrochloric acid at the ordinary temperature, and then allowing the mixture to remain during 6 hours; the liquid is then diluted, and allowed to remain for another 6 hours, when the precipitate is separated, washed, and dried. It crystallises from dilute alcohol in nodular aggregates of colourless prisms, and sinters at 210—220°, according to the rate of heating. A determination of its molecular weight in naphthalene gave the value 351 (calculated = 342). It behaves exactly like the parent substance towards concentrated sulphuric acid containing iron; if the amount of acid be such that no coloration is at first produced, the gradual development of a beautiful red tint is noticed and simultaneously of a green fluorescence.

Toxigenone, $C_{20}H_{26}O_3$ or $C_{19}H_{24}O_3$, is the name used by the author for a substance obtained by adding chromic acid mixture to a solution of anhydrodigitoxigenin in ten parts of hot acetic acid; it separates immediately in yellowish needles resembling sal-ammoniac. It is purified by dissolving it in chloroform, treating with blood-charcoal, and adding ether to the filtered liquid, when colourless, fern-like crystals separate. With concentrated sulphuric acid containing iron, a yellow coloration is gradually produced. When heated, it turns yellow at 220°, but does not melt even at 250°. Boiling dilute alkalis have no effect on the substance, which seems to be a ketone. Toxigenone is sparingly soluble in cold alcohol and acetic acid, but dissolves readily in concentrated sulphuric acid.

Digitaligenin has a molecular weight in naphthalene or acetic acid of 338—340, hence the earlier formulæ must be rejected, and one of the formulæ $C_{23}H_{32}O_3$ or $C_{22}H_{30}O_3$ probably represents its true composition. *Digitalose*, $C_7H_{14}O_5$, is the name suggested by the author for a sugar produced by the hydrolysis of digitalin; by treating the sugar mixture with bromine, δ-gluconic acid may be obtained and digitalonic acid, $C_7H_{14}O_6$, hence it is probable that δ-glucose and digitalose are products of hydrolysis of digitalin. Analysis of the calcium salt of digitalonic acid gave Ca = 9·35 per cent. and it was noticed that the salt, dried at 100°, burned without any preliminary fusion, thus differing from the calcium salt of the metameric digitoxosecarboxylic acid. On the basis of the foregoing results, the authors conclude that digitalin has the composition $C_{35}H_{56}O_{14}$ or $C_{36}H_{58}O_{14}(=C_{22}H_{30}O_3$ or $C_{23}H_{32}O_3+C_6H_{12}O_6+C_7H_{14}O_5)$. Molecular weight determinations of digitalin in glacial acetic acid gave very uncertain results.

Digitaligenin, when oxidised in acetic acid solution with chromic acid mixture, yields a substance, insoluble in water, which crystallises from alcohol, and appears to be identical with toxigenone.

The properties of French "digitaline crystallisée" correspond in many respects with those of the German preparations of "digitoxin," but certain marked differences between them are observable. Thus, analyses of the anhydrodigitoxigenins prepared from each indicate

that the French substance contains an additional $-CH_2-$ group; the French glucoside, deposited from its solution in chloroform, is at first amorphous and requires a temperature of 40° for its hydrolysis with alcoholic hydrogen chloride, whilst digitoxin separates from chloroform in a crystalline form, and is hydrolysed at the ordinary temperature with the foregoing agent. Again, the crystals of "digitaline crystal-lisée" show extinction parallel to their longest sides, whilst those of digitoxin, prepared under like conditions, extinguish when their longest sides make an angle of 14° with the plane of polarisation; for this reason and for several others, Prof. Groth pronounces them to be distinct substances.   A. L.

Gelsemic Acid. By ERNST SCHMIDT (*Arch. Pharm.*, 1898, **236**, 324—328).—Wormley (*Chem. Centr.*, 1870, 678) obtained a substance from the root of "*Gelsemium sempervirens*" which he called "gelsemic acid," and was said to be æsculin by Robbins (this Journ., 1877, ii, 344). Later, Virgil Coblentz (*Amer. J. Pharm.*, 1897) stated that gelsemic acid has the formula $C_{13}H_9O_3(OH)_2$. Some time since, the author had reason to believe that gelsemic acid was identical with β-methyl-æsculetin, a supposition which he now proves to be correct by showing that these two substances have the same melting point (202—203°), appearance, and solubility. Both contain one methoxyl-group as shown by Zeisel's method, and, on treatment with hydriodic acid, give æsculetin, $C_9H_6O_4$, crystallising from ethylic acetate in slender, white glistening needles which do not melt when heated to 250°.

Gelsemic acid must, therefore, be struck out of chemical literature. A tabulated comparison of the properties of gelsemic acid and β-methylæsculetin, and of the substance, $C_9H_6O_4$, obtained by the action of hydriodic acid on gelsemic acid and æsculetin, is given.
                                                                    A. W. C.

Hydrazo- and Azo-compounds of the Pyridine Series. By WILHELM MARCKWALD (*Ber.*, 1898, **31**, 2496—2497).—The α- and γ-chloro-derivatives of pyridine and quinoline readily react with hydrazine at about 150°. Thus 4-chloro-2 : 6-dimethylpyridine is converted by hydrazine hydrate at 150° into *4-lutidylhydrazine*, [2 : 6-*dimethylpyridine*-4-*hydrazine*], $NH_2 \cdot NH \cdot C_5NH_2Me_2$, which forms white crystals, and melts at 115—116°. Phenylhydrazine behaves in a similar manner, giving rise to a hydrazo-derivative which is converted by oxidation into an azo-compound. Further details will be given in a future communication.   A. H.

β-Diazopyridine and β-Diazoamidopyridine. By ERNST MOHR (*Ber.*, 1898, **31**, 2495—2496).—*Pyridineazoresorcinol*,
$$C_5NH_4 \cdot N \vdots N \cdot C_6H_3(OH)_2,$$
prepared from diazotised β-amidopyridine and resorcinol, crystal-lises in transparent, brown plates or prisms with violet reflex, becoming darker at 190°, finally melting at 218°.

β-Diazoamidopyridine, $C_5NH_4 \cdot N \vdots N \cdot NH \cdot C_5NH_4$, obtained by the action of sodium nitrite on β-amidopyridine hydrochloride, crystal-lises from benzene in pale yellow needles with violet reflex; it melts and evolves gas at 173—174°.

Benzylidene-β-pyridylhydrazine, $C_5NH_4 \cdot NH \cdot N:CHPh$, is prepared by reducing diazotised amidopyridine with tin and hydrochloric acid, and treating the hydrazine with benzaldehyde; it crystallises from dilute alcohol in aggregates of needles, and melts at 163—164°.

<div align="right">M. O. F.</div>

Formation of Condensed Nuclei with Para-linkings. By RICHARD STOERMER (*Ber.*, 1898, **31**, 2541—2543).—The *hydrochloride* of piperidoaldehyde, $C_7H_{14}ONCl$, is made by heating the corresponding acetal (Abstr., 1894, i, 556, and 1895, i, 479) with a large excess of hydrochloric acid which is afterwards removed in a vacuum; the salt, obtained by triturating the syrupy residue with ether, forms white crystals, and melts at 103°. The *platinochloride* crystallises in orange-yellow needles and melts at 121—122°; the *aurochloride* forms small, yellow crystals and melts at 109—111°. The free *base*, $C_5H_{10}:N \cdot CH_2 \cdot CHO$, may be crystallised from ether; it dissolves readily in alcohol and ether, and sparingly in water; it decomposes quickly in the free state. All attempts to cause internal condensation with elimination of water resulted in the resolution of the substance into piperidine and acetaldehyde. The *oxime*, $C_7H_{14}O_2N_2$, is obtained in white, flocculent masses, dissolves readily in alcohol and water, is insoluble in ether and chloroform, and melts at 135—136°; possibly it has the constitution $C_5H_{10}:NH{<}^{CH_2 \cdot CH}_{O}{>}N$. The *semicarbazone* crystallises well, is a powerful base, and melts at 76°.

<div align="right">A. L.</div>

Conversion of Nicotinic Acid into β-Amidopyridine. By THEODOR CURTIUS and ERNST MOHR (*Ber.*, 1898, **31**, 2493—2495).— Nicotinic *hydrazide*, $C_5NH_4 \cdot CO \cdot NH \cdot NH_2$, prepared from ethylic nicotinate and hydrazine hydrate, dissolves readily in water and in alcohol, but sparingly in benzene; it melts at 158—159°, and reduces Fehling's solution. The *hydrochloride* and *benzylidene* derivative melt at 227° and 149—152° respectively.

Nicotinazide, $C_5NH_4 \cdot CO \cdot N_3$, obtained by the action of sodium nitrite on the hydrochloride of nicotinic hydrazide, separates from ether as a white, crystalline mass with pungent odour, and melts at 47—48°. When the ethereal solution is heated with absolute alcohol in a reflux apparatus, *β-pyridylurethane*, $C_5NH_4 \cdot NH \cdot COOEt$, is produced; it crystallises from petroleum in aggregates of long, slender needles, and melts at 86—87°.

Di-β-pyridylcarbamide, $CO(NH \cdot C_5NH_4)_2$, is formed when nicotinazide is agitated with hot water until nitrogen ceases to be evolved; it crystallises from alcohol in groups of four-sided prisms, and melts at 217°, evolving gas.

β-Amidopyridine hydrochloride is produced when β-pyridylurethane is heated with fuming hydrochloric acid in a reflux apparatus, or when di-β-pyridylcarbamide is heated with the same agent, in a sealed tube, at 125°; the *platinochloride*, when crystallised from concentrated hydrochloric acid, has the composition $(C_5H_6N_2)_2, H_2PtCl_6 + 2HCl$, and blackens and intumesces at 239°.

<div align="right">M. O. F.</div>

Action of Alkylic Iodides on α-Methylindole in Alkaline Media. By ANTONIO PICCININI (*Gazzetta*, 1898, **28**, ii, 87—90).—On warming a mixture of α-methylindole with 20 per cent. potash and methylic iodide at 40° for 12 hours, the so-called pentamethyldihydroquinoline of Zatti and Ferratini (Abstr., 1892, 614) is obtained; on interrupting the operation, after three hours heating, the trimethylated base is obtained.

If ethylic iodide is used in place of methylic iodide, no pentethylated product is formed, but the bases, $C_{13}H_{17}N$ and $C_{13}H_{16}NEt$, described by Plancher (Abstr., 1898, i, 536).   W. J. P.

Behaviour of Dihydro-α-methylindole on Reduction with Hydrogen Iodide. By ANTONIO PICCININI and G. CAMOZZI (*Gazzetta*, 1898, **28**, ii, 91—100).—In order to prepare an octohydro-compound, the authors heated dihydro-α-indole with hydriodic acid and red phosphorus at 240° for 12 hours, but found that opening of the indole ring had occurred, with formation of *orthopropylaniline*, $C_9H_{13}N$; the new base is a colourless oil of aromatic odour boiling at 219°, and gives the isonitrile reaction. The *picrate*, $C_9H_{13}N,C_6H_2(NO_2)_3 \cdot OH$, crystallises in yellow needles melting at 151°, and the *hydrochloride*, $C_9H_{13}N,HCl$, in colourless needles melting at 173°; the base yields a diazo-compound with nitrous acid.

Orthopropylacetanilide, $C_9H_{12}NAc$, crystallises in colourless needles melting at 104—105°, and orthopropylbenzanilide in colourless prisms melting at 119°.   W. J. P.

Indigotin. By LEO MARCHLEWSKI and L. G. RADCLIFFE (*J. pr. Chem.*, 1898, [ii], **58**, 102—109).—This paper describes a more exact study of some reactions first described by O'Neill (*Mem. Manchester Phil. Soc.*, 1892), since deceased. When finely-powdered indigotin is dissolved in acetic acid, oxidised by the gradual addition of finely-powdered potassium permanganate, and washed with acetic acid, first pure and then containing sulphurous anhydride, a product is obtained which is insoluble in all ordinary solvents in the cold, decomposes when heated, and appears to be *diacetoxyindigotin*, $C_2(OAc)_2\left[<^{CO}_{NH}>C_6H_4\right]_2$. Boiling with water decomposes it into acetic acid, isatin, and indigotin; when treated with caustic soda in the cold, it yields sodium acetate, indigotin, and *di-isatic acid*, $C_{16}H_{14}N_2O_6$, which melts at 226—227°, loses $2H_2O$ when heated at 115°, forms a *silver* salt, $C_{16}H_{11}AgN_2O_5$, and a *bromo*-derivative, $C_{16}H_{12}Br_2N_2O_6$.   C. F. B.

Derivatives of Lepidine. By WILHELM KOENIGS (*Ber.*, 1898, **31**, 2364—2376).—*Dibromonitrolepidine*, obtained by brominating nitrolepidine in glacial acetic acid in the presence of fused sodium acetate at 100°, separates from ether or from benzene and petroleum in colourless crystals and melts at 114—115°. *Nitro-4'-quinolinealdehyde*, prepared by warming the dibromide with silver acetate in 60 per cent. acetic acid, melts at 175°, and crystallises from petroleum and benzene as a yellow powder.

Tribromonitrolepidine results from the action of excess of bromine on nitrolepidine ; it forms lustrous crystals and melts at 162° ; when heated with lead acetate in glacial acetic acid solution, it is converted into an acid which does not contain bromine. These results show that in both the di- and tri-bromonitrolepidines all the bromine atoms are in the side chain, and that their constitutions may be thus represented, $NO_2 \cdot C_9NH_5 \cdot CHBr_2$ and $NO_2 \cdot C_9NH_5 \cdot CBr_3$; the monobromo-derivative has not yet been obtained. *4'-Quinolylethanol (lepidinealkine ; 4-hydroxyethylquinoline)*, $C_9NH_6 \cdot CH_2 \cdot CH_2 \cdot OH$, is formed when lepidine is heated in sealed tubes at 100° with its own weight of 20 per cent. formaldehyde ; it can be purified by means of its *picrate*, which crystallises in yellow needles and melts at 155—157°. The *hydrochloride* is colourless and melts at 146° ; the *platinochloride*, $(C_{11}H_{11}NO)_2, H_2PtCl_6$, forms yellowish-red crystals and melts at 202°. The free base has not been obtained crystalline.

4'-Quinolylpropanediol, $C_9NH_6 \cdot C_3H_5(OH)_2$, is produced when twice as much formaldehyde is employed as in the former experiment ; the free base crystallises from ethylic acetate in colourless plates which melt at 127—129° ; it is soluble in the ordinary solvents, and separates from its aqueous solution in slender needles. The *hydrochloride* crystallises from alcohol and melts at 172°. The *platinochloride* crystallises with $2H_2O$ and melts at 200—202° ; the *picrate* melts at 170—172°. Quinolylpropanediol yields cinchonic acid on oxidation with nitric acid or sodium hypobromite ; when heated at 190° under diminished pressure, it gives off gas, and a sublimate of trioxymethylene is obtained. The *monobromhydrin*, obtained when quinolylpropanediol, is warmed with concentrated hydrobromic acid, crystallises from benzene in colourless plates and melts at 126—127°. When heated at 100—110°, or when boiled with alcohol or benzene, it is converted into the soluble hydrobromide of a base which does not contain bromine.

4'-Quinolylpropanediol di-iodohydrin hydriodide, produced on boiling together quinolylpropanediol, hydriodic acid, and red phosphorus, crystallises in golden-yellow needles, and melts and decomposes at 188°. The free *di-iodohydrin* is colourless, and melts and decomposes at 140°. The *moniodohydrin*, obtained from the mother liquor of the preceding compound, separates from its solutions in ether and ethylic acetate in colourless crystals, and melts at 117—119°.

4'-Propylquinoline results from the action of fuming hydriodic acid and red phosphorus on quinolylpropanediol at 160°. The *platinochloride* crystallises with $1\frac{1}{2}H_2O$ and melts and decomposes at 204° ; the *picrate* crystallises from alcohol in yellow needles and melts at 172—173°. The double chlorides of gold, mercury, cadmium, and zinc are precipitated in an oily form at first, but become crystalline on standing. The *methiodide*, which forms yellow crystals easily soluble in water, melts at 173°.

With the object of establishing the constitution of the quinolylpropanediol, the reduction of chloral-lepidine was studied. When treated with red phosphorus and fuming hydriodic acid at 160°, this substance yields an oily *4'-propylquinoline*, which should have the constitution $C_9NH_6 \cdot CH_2 \cdot CH_2 \cdot CH_3$; the platinochloride of this substance melts 8° lower than the corresponding salt of the preceding base, and

also differs from it in containing no water of crystallisation. The *picrate* of this base melts at 198°, that of the preceding base at 173°.

Quinolylpropanediol may have either of the following constitutions, $4'$-$C_9NH_6 \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, or $4'$-$C_9NH_6 \cdot CH(CH_2 \cdot OH)_2$, according as to whether the above propylquinolines are alike or different.

<div align="right">G. T. M.</div>

Preparation and Properties of Pentamethyldihydroquinoline from Indoles. By Antonio Piccinini (*Gazzetta*, 1898, 28, ii, 40—51).

—The most convenient method of preparing the pentamethyldihydro-quinoline of Zatti and Ferratini (Abstr., 1892, 614) is by treating trimethyl- or tetramethyl-dihydroquinoline with potash and methylic iodide in aqueous solution at about 40°; after distilling off the excess of methylic iodide, the base is purified by ether, conversion into sulphate and distillation in a current of steam. The base distils at 171—172° under 46 mm. pressure, and in a current of hydrogen at 268—269° under 750 mm. pressure; the *picrate*,

$$C_{14}H_{19}N,C_6H_2(NO_2)_3 \cdot OH,$$
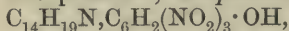
crystallises in golden scales melting at 128—129°, and the *hydriodide* in colourless prisms melting at 178—179°. The *aurichloride*, $C_{14}H_{19}N,HAuCl_4$, crystallises in long needles melting and decomposing at 152—153°.

On heating pentamethyldihydroquinoline with methylic iodide at 100°, it yields the methiodide, $C_{15}H_{22}NI$, which crystallises in colourless needles melting at 180°, and is identical with the product described by Zatti and Ferratini (*loc. cit.*) as melting at 172°. When treated with potash and distilled in a current of steam, an oily *base*,

$$C_{13}H_{16}Me_2N \cdot OH,$$
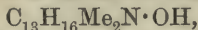
the hydroxide of the substituted ammonium, distils; the *aurochloride*, $C_{15}H_{19}N,AuCl_4$, crystallises in yellow scales melting at 142—145°, and the *picrate*, $C_{15}H_{22}NO \cdot C_6H_2(NO_2)_3$, forms golden scales melting at 121—122°.

On decomposing the methiodide, $C_{15}H_{22}NI$, with potash in the cold, a *hydroxide*, $C_{15}H_{22}N \cdot OH$, separates, which crystallises from alcohol in large prisms melting at 73—74°; the *aurichloride*, $C_{15}H_{22}NAuCl_4$, crystallises in leaflets melting at 164—165°, and the picrate, $C_{15}H_{22}NO \cdot C_6H_2(NO_2)_3$, forms yellow scales melting at 129—130°. The solid base is converted into its liquid isomeride by distillation in a current of steam, and the same change gradually occurs spontaneously.

<div align="right">W. J. P.</div>

Constitution of Hydroquinolines from Indoles. By Antonio Piccinini (*Gazzetta*, 1898, 28, ii, 51—67).

—On crystallising Ferratini's so-called secondary dimethyltetrahydroquinoline (Abstr., 1893, i, 602), $C_{11}H_{15}N$, with tartaric acid, it yields the *tartrate* of the lævo-component in large, colourless prisms melting at 85—86°; the *hydrochloride*, $C_{11}H_{15}N,HCl$, of the lævo-base melts at 203—204°, whilst that of the racemic base melts at 198—199°, and has the specific rotation $[a]_D = -15\cdot6°$ in aqueous solution. The base, therefore, has the constitution $C_6H_4 \underset{NH-}{\overset{CMe_2}{<}} CHMe$, and is an indole derivative.

On oxidising tetramethyldihydroquinoline with alkaline perman-

ganate in the cold, and extracting with ether, a mixture of the tri-methylindolinone, $C_6H_4\underset{NMe}{\overset{CMe_2}{<}}>CO$ (Brunner, Abstr., 1896, i, 625), and a compound of the composition $C_{24}H_{30}N_2O_2$, is obtained; the latter is a neutral substance which crystallises in colourless prisms melting at 124°, and its molecular weight was determined in freezing benzene. The so-called trimethyldihydroquinoline, therefore, has the constitution $C_6H_4\underset{NMe}{\overset{CMe_2}{<}}>C{:}CH_2$.

Pentamethyldihydroquinoline, $C_{14}H_{19}N$, when oxidised with alkaline permanganate, yields the same trimethylindolinone, and has, therefore, the constitution $C_6H_4\underset{NMe}{\overset{CMe_2}{<}}>C{:}CMe_2$.

On distilling α-methyldihydroindole hydrochloride with zinc dust, methylketol and quinoline are obtained, so that the formation of quinoline derivatives, on similarly treating Ferratini's secondary di-methyltetrahydroquinoline, does not prove the latter to contain a quinoline nucleus.   W. J. P.

Stereoisomerism in Piperazine and Ethylenediamine Deriva-tives. By WILLEM VAN RIJN (*Chem. Centr.*, 1898, i, 380—381; from *Ned. Tijdsch. Pharm.*, 10, 5—16).—Attempts to obtain stereoisomerides depending on the presence of two asymmetric nitrogen atoms in the cases of derivatives of piperazine and methylethylpropylethylene-diamine failed. Piperazonium bases containing four alkyl groups of the hexahydroterephthalic acid type cannot be prepared, as only one nitrogen atom is capable of combining with an alkylic haloid, and although the compounds thus formed can unite with an acid, the authors were unable to obtain the isomeric compounds

$$\underset{H}{\overset{R}{I}}{>}N{<}\underset{CH_2\cdot CH_2}{\overset{CH_2\cdot CH_2}{}}>N\underset{R_1}{\overset{R}{}} Cl \quad \underset{H}{\overset{R}{Cl}}{>}N{<}\underset{CH_2\cdot CH_2}{\overset{CH_2\cdot CH_2}{}}>N\underset{R_1}{\overset{R}{}} I.$$
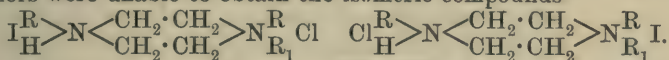
Dibenzylpiperazine, $CH_2Ph\cdot N{<}\underset{CH_2\cdot CH_2}{\overset{CH_2\cdot CH_2}{}}>N\cdot CH_2Ph$, is prepared by heating molecular proportions of ethylene bromide and benzylamine, or, better, by the action of benzylic chloride on piperazine; it crystal-lises from alcohol in needles, melts at 91—92°, is insoluble in water, soluble in ether, alcohol, chloroform, benzene, light petroleum, and carbon bisulphide. The *chloride* crystallises in plates, is slightly soluble in water, and gives precipitates with potassium dichromate, potassium ferrocyanide, auric chloride, and platinic chloride. The nitrate crystallises in leaflets and melts at 155°; the bromide crystal-lises in small needles, and the sulphate is very easily soluble. The author also prepared diphenyldibenzylethylenediamine by the action of benzylic chloride and concentrated potassium hydroxide solution on diphenylethylenediamine; it crystallises from benzene in colourless crys-tals and melts at 134—135°; a nitroso-derivative could not be obtained.

The compounds of dibenzylpiperidine with one molecule of an alkylic haloid are easily prepared by warming a mixture of the com-ponents on the water-bath. *Dibenzylpiperazine methiodide* crystallises from alcohol in small prisms and melts at 217°. *Dibenzylpiperidine ethiodide* crystallises from hot water in white needles, melts at 197°, is

soluble in alcohol, methylic alcohol, chloroform, and carbon bisulphide, and very slightly soluble in ether, acetone, light petroleum, and benzene. *Dibenzylpiperazine propiodide* forms yellow needles, decomposes at 260°, and is slightly soluble in alcohol. *Dibenzylpiperidine isobutobromide* crystallises from hot water in colourless crystals, melts at 195—196°, is soluble in alcohol, chloroform, and acetone, and insoluble in carbon bisulphide, ether, benzene, and light petroleum.   E. W. W.

Isorosindones. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1898, **31**, 2477—2482. Compare Abstr., 1898, i, 334).—Phosphorus pentachloride converts the alkylisorosindones into unstable dichlorides which lose alkylic chloride when heated, yielding chloronaphthaphenazines (compare Abstr., 1898, i, 383).

Chlorethylnaphthaphenazonium chloride, $C_6H_3Cl\ll^{N---}_{N\,EtCl}>C_{10}H_6$, prepared by heating ethylisorosindone with phosphorus oxychloride and phosphorus pentachloride on the water-bath, crystallises from alcohol in brownish aggregates; it dissolves readily in water, and the alcoholic solution has a feeble, greenish-brown fluorescence. The *platinochloride, aurichloride,* and *nitrate* crystallise in needles, and the *mercurichloride* in leaflets. *Chlorophenonaphthazine,*

$C_6H_3Cl\ll^N_N>C_{10}H_6$, obtained by heating the foregoing phenazonium chloride at 170—180°, crystallises from benzene in yellow needles; it melts at 191°, and the solution in concentrated sulphuric acid is cherry red.

Methylisorosindone, $O<^{C_6H_3\cdot N}_{NMe\cdot C_{10}H_{16}}$, is produced on heating an alcoholic solution of a methyl-β-naphthylamine salt with nitrosophenol and an acid; it separates from a mixture of benzene and petroleum in black crystals having a metallic reflex, and melts at 212—214°. The *hydrochloride, hydrobromide,* and *hydriodide* are dissociated by hot water.

Benzylisorosindone, $O<^{C_6H_3=N}_{N(CH_2Ph)}>C_{10}H_6$, prepared from benzyl-β-naphthylamine and nitrosophenol, crystallises in brownish-violet needles and melts at 210°; the solution in concentrated sulphuric acid is bluish-violet. The *hydrochloride, hydrobromide,* and *hydriodide* are crystalline.

β-Naphthylisorosindone, prepared from β-dinaphthylamine and nitrosophenol, separates from pyridine in black crystals having a metallic reflex; the solution in concentrated sulphuric acid is deep bluish-violet. The *hydrochloride, hydrobromide,* and *hydriodide* are crystalline.   M. O. F.

Hydroxyrosindines. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1898, **31**, 2482—2485. Compare Abstr., 1895, i, 611).— Symmetrical *hydroxyrosindone,* $O<^{C_{10}H_5\cdot N}_{NPh---}>C_6H_3\cdot OH$, otherwise called naphthasafranol, was first obtained from B$_2$-amidophenylrosinduline (Abstr., 1893, i, 335), and the methylic ether has been recently

prepared from isorosindone methiodide by the action of alcoholic potash (Abstr., 1898, i, 338); although naphthasafranol is regenerated when this compound is heated with concentrated hydrochloric acid, methylic iodide converts it into a methylic ether which differs from the one which has been already described. Examination has shown this substance to be identical with the methoxyisorosindone described as melting at 274° (Abstr., 1897, i, 171).

Naphthasafranol *methylic ether* crystallises from pyridine in slender, deep red prisms or needles, and melts at 308°; the solution in concentrated acid is reddish-violet. The *ethylic ether* melts at 269°.

M. O. F.

Synthesis of Indulines. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1898, **31**, 2485—2489).—*Dinaphthaphenylsafranine*,

$$NPh<\begin{matrix}C_{10}H_5:N\\NPh\end{matrix}>C_{10}H_6,$$
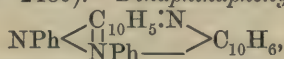
formerly prepared from α-amidoazonaphthalene hydrochloride, or from aniline and benzeneazo-α-dinaphthylamine, is readily obtained by heating nitrosophenyl-α-naphthylamine hydrochloride and phenyl-β-naphthylamine with glacial acetic acid on the water-bath; it crystallises from boiling pyridine in bulky, dull gold needles, and melts at 268°. When the hydrochloride is heated with aqueous ammonia (1 mol.) and alcoholic ammonia (15—20 mols.), one phenylic group is eliminated, and dinaphthaposafranine (naphthinduline),

$$NH<\begin{matrix}C_{10}H_5:N\\NPh\end{matrix}>C_{10}H_6,\text{ is produced.}$$
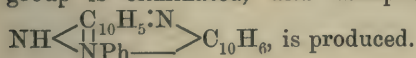
Ethyldinaphthaphenylaposafranine, $NPh<\begin{matrix}C_{10}H_5:N\\NEt-\end{matrix}>C_{10}H_6$, obtained from nitrosophenyl-α-naphthylamine hydrochloride and ethyl-β-naphthylamine, crystallises from pyridine in black prisms having a metallic reflex, and melts at 254—255°. A mixture of glacial acetic and concentrated hydrochloric acids at 210°, eliminates aniline, and gives rise to *ethyldinaphthaposafranine*, $O<\begin{matrix}C_{10}H_5:N\\NEt-\end{matrix}>C_{10}H_6$, which crystallises from alcohol in golden needles, and melts at 247°; the *hydrochloride* forms greenish prisms, and the *nitrate* crystallises from alcohol in red needles.

M. O. F.

3-Acetamido-β-naphthaquinone and some of its Derivatives. By FRIEDRICH KEHRMANN and FRITZ ZIMMERLI (*Ber.*, 1898, **31**, 2405—2412).—*3-Acetamidonaphthaquinol*, $C_6H_4<\begin{matrix}C(OH):C\cdot OH\\CH=C\cdot NHAc\end{matrix}$, which is formed when the triacetyl derivative is heated with the calculated amount of dilute aqueous soda, decomposes at about 170°. The corresponding *quinone*, obtained by the action of chromic acid mixture on the solution of the quinol, crystallises in dark brownish-red needles, which melt at 214—216° and form a dark blood-red solution in alcohol. 4-*Chloro-3-acetamido*-1 : 2-*naphthaquinone*,
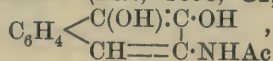
$$C_6H_4<\begin{matrix}CO\cdot CO\\CCl\cdot CNHAc\end{matrix},$$
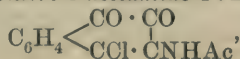
is prepared by treating the foregoing compound with hydrochloric acid, and oxidising the quinol which is formed by chromic acid mixture. It forms well developed, garnet-red prisms, which melt and decompose at about 170°, and reacts readily with orthophenylene-diamine hydrochloride to form 6-*chloro-5-acetamidonaphthaphenazine*,

$$C_6H_4 \begin{matrix} N:\overset{|}{C}\cdot C_6H_4 \text{---} \\ N:C\cdot C(NHAc) \end{matrix} CCl,$$ which crystallises in pale yellow needles

and melts at 292°.

4-Chloro-3-acetamido-1 : 2-naphthaquinone is readily converted by dilute aqueous soda into 2-*hydroxy-3-acetamido-*1 : 4-*naphthaquinone*,

$$C_6H_4 \begin{matrix} CO\cdot C\cdot OH \\ CO\cdot C\cdot NHAc \end{matrix},$$ which is identical with the acetamidonaphtha-

linic acid described by Kehrmann and Weichardt (Abstr., 1889, 1197). This compound is probably formed by intramolecular change from the hydroxy-1 : 2-naphthaquinone, which is doubtless the first product.

3-Acetamido-1 : 2-naphthaquinone is converted by ammonia and monamines into substances which are at the same time orthodiamines and quinones, and are therefore capable of yielding substances which contain the characteristic groups of imidazoles and azines.

3-*Acetamido-4-amido-*1 : 2-*naphthaquinone*, $$C_6H_4 \begin{matrix} CO\text{---}CO \\ CNH_2:C\cdot NHAc \end{matrix}$$

formed by the action of ammonia on acetamidonaphthaquinone, crystallises in chocolate-coloured needles melting at 222°.

3-*Acetamido-4-methylamido-*1 : 2-*naphthaquinone* is obtained by the action of methylamine on the acetamidoquinone, and forms dark reddish-brown crystals melting at 245—246°; it is converted by aqueous soda into acetamidohydroxy-1 : 4-naphthaquinone. The foregoing compound reacts with orthophenylenediamine to form *dimethyl-imidazolonenaphthaphenazine*, $$|C_6H_4 \begin{matrix} N:C\text{------}C\text{---}N \\ N:C\cdot C_6H_4\cdot C\cdot NMe \end{matrix} CMe,$$ which cyystallises in orange-coloured needles melting at 264°. The monacid salts are not dissociated by water.

3-*Acetamido-4-anilido-*1 : 2-*naphthaquinone* forms dark brown, glistening crystals melting at about 308°. When the solution in acetic acid is boiled, it is converted into *phenylmethyl-3 : 4-imidazolone-1 : 2-naphthaquinone*, $$CO \begin{matrix} CO\text{---}C\text{---}N \\ C_6H_4\cdot C\cdot NPh \end{matrix} CMe,$$ which crystallises in light, garnet-red needles, and melts at 305—306°.

3-Acetamidonaphthaquinone reacts with orthophenylenediamine to form 5-*acetamidonaphthophenazine*, $$C_6H_4 \begin{matrix} N:C\cdot C_6H_4\text{---} \\ N:C\cdot C(NHAc) \end{matrix} CH,$$ which crystallises in pale yellow needles melting at 240°, and is not fluorescent. Hydrochloric acid converts it into the 5-*amidonaphthaphenazine hydrochloride* which crystallises in small, almost colourless needles. The free *amido*-compound forms short, blood-red prisms melting at 198—199°. This compound is the third isomeride of amidonaphthaphenazine ; a fourth is described in the following abstract.

5-*Hydroxynaphthaphenazine*, $$C_6H_4 \begin{matrix} N:C\cdot C_6H_4\text{---} \\ N:C\cdot C(OH) \end{matrix} CH,$$ which is

formed when the amido-compound is heated with 5 per cent. sulphuric acid at 140—150°, crystallises in lemon-yellow needles melting at 199°.

<div align="right">A. H.</div>

3′-Acetamido-β-naphthaquinone and some of its Derivatives. By FRIEDRICH KEHRMANN and M. MATIS (*Ber.*, 1898, **31**, 2413—2418. Compare the foregoing abstract).—1 : 3-Dinitro-β-naphthol is converted by reduction and treatment of the product with acetic anhydride into triacetyldiamido-β-naphthol, and this is partially hydrolysed by dilute aqueous soda, yielding *diacetamido-β-naphthol*, $C_{14}H_{14}N_2O_3$, which crystallises in almost colourless needles melting at 235°. On oxidation with chromic acid mixture, the naphthol is converted into 3′-*acetamido-β-naphthaquinone*,

$$CH \cdot CH \cdot C \cdot CO \cdot CO$$
$$NHAc \cdot C \!\!-\!\!-\!\! CH \cdot C \cdot CH \!\!:\!\! CH'$$
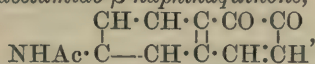
which forms dark red, granular crystals, and decomposes at 180°. This substance is much more closely allied to β-naphthaquinone both in appearance and chemical behaviour than is the isomeric compound previously described. With orthophenylenediamine hydrochloride, it yields 3″-*acetamidonaphthaphenazine*, $C_{18}H_{13}N_3O$, which crystallises in long, pale yellow needles melting at 274°; on treatment with sulphuric acid, it is converted into 3″-*amidonaphthaphenazine*,

$$C_6H_4 \!\!<\!\!\genfrac{}{}{0pt}{}{N}{N}\!\!>\!\! C_6H_2 \!:\! C_6H_3 \cdot NH_2,$$
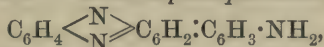
which crystallises in orange-coloured, lustrous plates melting at 217°. Aniline converts the quinone into 4-*anilido-3-acetamido-β-naphthaquinone*, $NHAc \cdot C_6H_3 \!\!<\!\!\genfrac{}{}{0pt}{}{CO\!-\!-\!-\!CO}{C(NHPh) \!:\! CH}$, which is a red, crystalline powder almost insoluble in alcohol and melting and decomposing at 282°. 3′-*Acetamido-β-naphthaquinonemonoxime*, crystallises in pale yellow needles which decompose at 230°. A dioxime could not be prepared. 3′-*Amido-β-naphthaquinonemonoxime* is precipitated in red needles when the alkali solution of the acetyloxime is boiled and acidified with acetic acid, but these soon change into yellow crystals. When these are redissolved in alkali and again precipitated by acid, the red needles are again produced. It crystallises from alcohol in orange-coloured plates which decompose at 190°. These two modifications of the oxime correspond in their properties with those of the oxime of 4-amido-β-naphthaquinone. The isomerism may possibly be due to the presence of a nitroso-group in one form and an isonitroso-group in the other.

<div align="right">A. H.</div>

Azonium Compounds from Benzil. III. By FRIEDRICH KEHRMANN and C. NATCHEFF (*Ber.*, 1898, **31**, 2425—2428. Compare Abstr., 1891, 945).—The *nitrate* of the azonium compound formed from benzil and orthamidodiphenylamine crystallises in sulphur yellow needles, has a bitter taste, and melts at 172°.

The compound from benzil and diamidodiphenylamine yields a *chloride*, $C_{26}H_{20}N_3Cl$, which forms lustrous, ruby-red crystals. The *acetyl* derivative, $C_{28}H_{22}N_3OCl$, crystallises in golden-yellow needles.

Orthamidodiphenylamine yields, with nitrobenzil, a base, $C_{26}H_{19}N_3O_3$,

which crystallises in orange-yellow needles melting at 169°, and can also be obtained as a brick-red, flocculent precipitate. The *ferrichloride*, $C_{26}H_{18}N_3O_2FeCl_4$, forms readily soluble, yellow crystals. Benzil condenses with nitrophenylorthophenylenediamine to form a compound, $C_{26}H_{19}N_3O_3$, which separates in lemon-yellow, crystalline granules, and melts at 161°; an intermediate *compound*, $CPhO\cdot CPh\colon N\cdot C_6H_3(NO_2)\cdot NHPh$, is first formed which has no basic properties and crystallises in long, pale yellow needles melting at about 200°.

The authors have recently obtained experimental evidence that these compounds are not true azonium bases, and this will form the subject of a future communication.   A. H.

The Azonium Compounds prepared from β-Naphthaquinone-4-sulphonic Acid and Phenylorthophenylenediamine. By FRIEDRICH KEHRMANN and C. LOCHER (*Ber.*, 1898, **31**, 2428—2437. Compare Abstr., 1896, i, 700).—The sulphonic acids of both phenylnaphthaphenazonium and phenylisonaphthaphenazonium exist in the form of anhydrides, the elements of water having been eliminated from the azonium hydroxyl and the sulphonic group. Phenylnaphthaphenazonium-6-sulphonic acid readily reacts with alkalis, amines, hydroxylamine, and benzenesulphinic acid, the sulphonic group being in all cases eliminated. Caustic soda converts it into rosindone, whilst ammonia produces rosinduline; methylamine acts in a similar manner to ammonia, and converts the acid into methylrosinduline, the *nitrate* of which crystallises in red, lustrous plates, which are almost insoluble in cold water and decompose at about 257°, whilst the *aurichloride* forms small, garnet red, insoluble needles. Aniline also behaves in a similar manner, yielding phenylrosinduline. Acetylparaphenylenediamine reacts with the sulphonic acid to produce *acetamidophenylrosinduline chloride*,

$$\underset{NHAc\cdot C_6H_4\cdot NH\cdot C\colon CH\cdot C\colon NPhCl}{\overset{C_6H_4\cdot C\colon N}{\diagdown}}\!\!>\!\!C_6H_4,$$
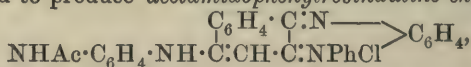
which crystallises in greyish-brown needles having a metallic lustre. When this salt is decomposed by sodium carbonate, the anhydride of the free *base* is formed, $C_{30}H_{22}N_4O$, and separates in brown crystals. On heating the substance with 50 per cent. sulphuric acid, it is converted into *amidophenylrosinduline sulphate*, $C_6H_4\!\!<\!\!\overset{NH\text{——}C_{10}H_5\colon N}{\underset{NH_3\cdot SO_4\cdot NPh\text{—}C_6H_4}{}}$; the corresponding *chloride* crystallises in bluish-violet needles with a metallic lustre and forms a *platinochloride*, $(C_{28}H_{22}N_4)_2,PtCl_6$, which is a dark violet, crystalline precipitate, and is quite insoluble in water. Hydroxylamine converts the sulphonic acid into a compound which is probably 6-*oxamidophenylnaphthaphenazonium anhydride*,

$$O\!\!<\!\!\overset{NH\cdot C_{10}H_5\colon N}{\underset{\text{——}NPh\text{—}C_6H_4}{}}$$
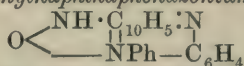
This substance crystallises in small, ruby-red prisms, and decomposes at 233°; it is insoluble in alkalis, and is not attacked by acetic anhydride. Benzenesulphinic acid also reacts with the sulphonic acid, forming a phenylsulphone *derivative*,

$$SO_2Ph\cdot C_{10}H_5\!\!\lll\!\!\overset{N\text{——}}{\underset{NPh(OH)}{}}\!\!>\!\!C_6H_4,$$
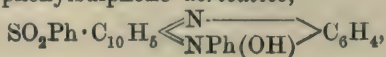
which resembles rosindone in physical properties, but cannot have a paraquinoid constitution, so that its existence is a strong argument in favour of Nietzki's orthoquinoid formula. It forms hard, reddish-brown crystals, and melts at 287°.

Phenylisonaphthaphenazonium-9-sulphonic acid reacts with amines in a manner different from its isomeride, violet or blue sulphonic acids of the isorosindulines being obtained; 2-*dimethylamidophenyl-isonaphthaphenazonium-4'-sulphonic anhydride*, O——NPh—$C_6H_3 \cdot NMe_2$, $SO_2 \cdot C_{10}H_5 \cdot N$ is formed by the action of dimethylamine on the isosulphonic acid, and crystallises in small, dark violet needles which have a coppery lustre.

The mother liquors of the two azonium-sulphonic acids, to which reference has already been made, contain a *compound* which crystallises in long, dark violet needles melting at 212°; this is probably 2'-*hydroxyrosindone*, $O < \frac{NPh\text{——}C_6H_4}{C_{10}H_4(OH):N}$, although its constitution cannot be considered as definitely ascertained.   A. H.

Action of Alkylorthodiamines on Tetrahydroxyquinone and Rhodizonic Acid. By FRIEDRICH KEHRMANN and ALBERT DURET (*Ber.*, 1898, 31, 2437—2442).

—Tetrahydroxyquinone readily undergoes condensation with phenylorthophenylenediamine hydrochloride to form 1 : 2 : 4-*trihydroxyphenylaposafranone*, $O < \frac{NPh \cdot C_6H_4}{C_6H_4(OH)_3} > N$, which crystallises in brownish-green, dichroic needles with a steel-blue lustre; the *triacetate* crystallises in reddish-violet needles, and decomposes at 220—225°. The trihydroxy-compound dissolves in aqueous alkalis with a red coloration, which soon becomes yellow, and acids then precipitate 2-*hydroxyphenylaposafranonequinone*, $C_{18}H_{20}N_2O_4$, crystallising in tablets which have a dark green, metallic lustre and decompose at about 275°. It has not yet been ascertained whether this substance is a para- or an ortho-quinone. Dilute nitric acid converts the trihydroxy-compound into a *substance*, $C_{16}H_{10}N_2O_4$, which crystallises in pale yellow, microscopic needles, and is readily soluble in aqueous soda; its constitution has not been determined.

1 : 2 : 4-*Trihydroxymethylaposafranone*, $O < \frac{NMe \cdot C_6H_4}{C_6H_4(OH)_3} > N$, obtained by the condensation of tetrahydroxyquinone with methylorthophenylenediamine, crystallises in green plates which have a faint metallic lustre, and decompose at 250—255°.

Rhodizonic acid undergoes a complicated reaction with phenylorthophenylenediamine, yielding trihydroxyaposafranone, along with a *compound*, $C_{30}H_{18}N_4O_2$, which forms crystalline granules having a violet, metallic lustre, and yielding a crystalline *hydrochloride*; this substance seems to be formed from 1 mol. of rhodizonic acid and 2 of the base, and probably has the constitution

$$C_6H_4 < \frac{N\text{==}C \cdot C:N\text{--}}{\underset{O\text{--} \cdot C:C \cdot O}{NPh:C \quad C:NPh}} > C_6H_4.$$
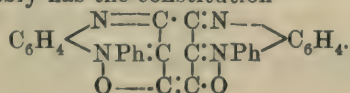
A. H.

An Isomeride of Diphenylfluorindine. By FRIEDRICH KEHRMANN and ALBERT DURET (*Ber.*, 1898, **31**, 2442—2444. Compare Abstr., 1896, i, 631).—The chloride of isodiphenylfluorindine yields a base which contains no oxygen, and probably has the constitution $C_6H_4\!<\!\!{}^{NPh}_{-N}\!\!\overline{}\!\!>\!\!C_6H_2\!<\!\!{}^{N\overline{}}_{NPh}\!\!>\!\!C_6H_4$, so that it is isomeric with diphenyl-fluorindine. On adding ammonia to the chloride, it is precipitated in grass-green, microscopic crystals. The *ferrichloride*, $C_{30}H_{22}N_4Cl_2,FeCl_3$, crystallises in dark blue tablets, and the *platinochloride* is an indigo-blue, crystalline precipitate which is insoluble in water. The *dichromate* is also an insoluble crystalline precipitate, whilst the *aurichloride* is a flocculent powder.   A. H.
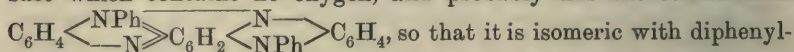
Hydroxytriazolecarboxylic Acid and Hydroxytriazole. By WILHELM MANCHOT (*Ber.*, 1898, **31**, 2444—2447).—*3-Hydroxytriazole-5-carboxylic acid*, $\begin{smallmatrix}C(OH)\cdot N\\ \| \quad\quad\quad\\ N\text{----}NH\end{smallmatrix}\!\!>\!\!C\cdot COOH$, prepared by heating diazotriazolecarboxylic acid with 12—15 times its weight of dilute sulphuric or nitric acid until the evolution of nitrogen is at an end, is sparingly soluble in cold water or alcohol, but dissolves readily in the hot liquids ; it crystallises from water in small, apiculate, prismatic needles frequently aggregated to rosettes. It contains $1H_2O$, which is driven off with difficulty at 120° ; it then melts and decomposes at 205°. It is a fairly strong acid, and, with silver nitrate, its aqueous solution yields a white, and, with copper sulphate, a bluish-green precipitate.

3-Hydroxytriazole, which is easily prepared from the foregoing acid by heating it at its melting point, agrees in properties with the compound prepared by Widman and Cleve (Abstr., 1898, i, 335) ; it gives a red coloration when mixed with an alkaline solution of diazobenzenesulphonic acid, thus exhibiting a phenolic character, and supplying further evidence of the aromatic nature of the triazole nucleus.

If the decomposition of the above diazo-compounds has been effected by means of nitric acid, the mother liquors, on evaporation, leave a residue which gives a yellow precipitate with silver nitrate, and forms a red solution with alkalis.

The author makes a preliminary announcement of the fact that, whilst reduction of diazotriazolecarboxylic acid to the corresponding hydrazine is difficult to accomplish, he has succeeded in obtaining a satisfactory yield of benzyltriazylhydrazone (m. p. = 225°).   A. L.

Diketones of Tetrahydro-β-oxazole derived from the Phenyl-urethanes of some Hydroxy-acids. By EUGÈNE LAMBLING (*Compt. rend.*, 1898, **127**, 188—190).—It has been previously shown (this vol., i, 52) that the action of phenylcarbimide on compounds of the type $COOR^1\cdot CHR\cdot OH$ gives rise to phenylurethanes of the formula $COOR^1\cdot CHR\cdot O\cdot CO\cdot NHPh$, from which the corresponding acids may be obtained by successive treatment with alkali and acid. When boiled with water, these acids yield anhydrides of the constitution $CO\!<\!\!{}^{CHR\cdot O}_{NPh\cdot CO}$, which may be regarded as diketo-derivatives of tetra-

hydro-β-oxazole. The following derivatives were thus obtained from the phenylurethanes of lactic, trichlorolactic, glycollic, phenylglycollic, and α-hydroxyisobutyric acids.
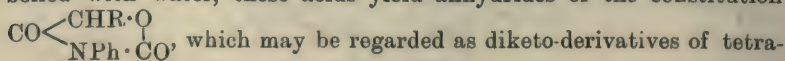
The *diketone*, $CO<^{CHMe\cdot O}_{NPh-CO}>$, crystallises in microscopic needles melting at 141°, and is slightly soluble in cold, and more soluble in boiling, water, soluble in alcohol and ether. It is insoluble in a cold concentrated solution of sodium carbonate, but, on warming, the sodium salt of the phenylurethane of lactic acid is regenerated. This diketone has also been prepared by Travers, who obtained from it an acid to which he ascribed the constitution $OH\cdot CHMe\cdot CO\cdot NPh\cdot COOH$, a formula which is not in accordance with the reactions studied by the author.

The *diketone*, $CO<^{CH(CHCl_2)}_{NPh-CO}>O$, crystallises from boiling alcohol in slender needles melting at 202°. It may be prepared by the general method indicated above, and also by the hydrolysis of the phenylurethane of trichlorolactonitrile, or of the *compound*

$$CHCl_2\cdot CH(CN)\cdot O\cdot CO\cdot NHPh.$$
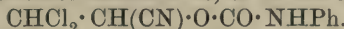
The latter is obtained by the action of aqueous soda on trichlorolactonitrile phenylurethane, and crystallises in microscopic needles melting at 150°. In this reaction, dichloracetanilide, $CHCl_2\cdot CO\cdot NHPh$, crystallising in needles melting at 116°, is also produced.

The *diketones*, $CO<^{CH_2\cdot O}_{NPh\cdot CO}>$, $CO<^{CHPh\cdot O}_{NPh-CO}>$, and $CO<^{CMe_2\cdot O}_{NPh-CO}>$, are crystalline compounds melting at 121°, 122°, and 118—119° respectively, and, when boiled with concentrated sodium carbonate solution, yield the phenylurethanes from which they are derived.

Experiments made with the phenylurethanes derived from ethylic β-hydroxybutyrate and from methylic salicylate, which might be expected to yield closed chain compounds of six elements, have hitherto yielded no definite result. N. L.

Benzisothiazole. By SIEGMUND GABRIEL and ERNST LEUPOLD (*Ber.*, 1898, **31**, 2185—2187).—When benzisothiazole, $C_6H_4<^{CH}_{N}>S$ (Abstr., 1895, i, 432; 1896, i, 215), is heated with phenylhydrazine, ammonia, hydrogen sulphide, and benzene are evolved, and orthamidobenzaldehydephenylhydrazone, $NH_2\cdot C_6H_4\cdot CH\!:\!N\cdot NHPh$ (Eliasberg and Friedländer, Abstr., 1892, 1106), is formed. When it is heated with hydrazine hydrate, ammonium sulphide is evolved, and *orthamidobenzylideneazone*, $(NH_2\cdot C_6H_4\cdot CH\!:)_2N_2$, is obtained; this can also be prepared by heating a solution of orthamidobenzaldehyde with hydrazine hydrate; it is a yellow, crystalline substance, which melts and decomposes at about 244° and has feebly basic properties; the yellow *hydrochloride*, with 1HCl, was prepared and analysed. C. F. B.

New Creatinine Derivative. By WILLIAM KRAMM (*Chem. Centr.*, 1898, i, 37—38; *from Centr. med. Wiss.*, **35**, 785—787).—By treating

urine with sodium nitroprusside and sodium hydroxide solution and, as soon as the colour changes to yellow, adding acetic acid and shaking vigorously, a crystalline precipitate of *nitrosocreatinine*, $C_4H_6N_4O_2$, is obtained. It is soluble in dilute mineral acids, in dilute sodium hydroxide solution, and in excess of ammonia; it is precipitated from its yellow alkaline solutions by acetic acid or carbonic anhydride, and gives a silver compound which is insoluble in water. Nitrosocreatinine may also be prepared from a solution of pure creatinine.

E. W. W.

Allocaffeine. By HENRY A. TORREY (*Ber.*, 1898, **31**, 2159—2162). —Allocaffeine, $C_8H_9N_3O_5$, prepared from tetramethyluric acid (E. Fischer, Abstr., 1898, i, 180) was boiled with plenty of water; carbonic anhydride was evolved, and the allocaffeine went into solution. The product, *allocaffuric acid*, $C_7H_{11}N_3O_4$, left on evaporating the water, was crystallised from ethylic acetate; the crystals, when they first separated, melted at 158°, but after remaining for several days in contact with the mother liquor, they melted at 164—165°. When warmed with baryta water for a few minutes at 40°, the acid is decomposed into dimethylcarbamide and a *monomethylamide* of *mesoxalic acid*; this substance, which has acid properties and forms an insoluble barium salt, was only obtained as a syrup, but its *phenylhydrazone*, $C_{10}H_{11}N_3O_3$, which melts and decomposes at about 158°, was obtained in yellow crystals and analysed; when it is heated with 30 per cent. caustic soda, a sodium salt separates at first, but on heating to 100° a new product, $C_9H_{11}N_3O$, melting at 205—209° is obtained. If allocaffuric acid is boiled with baryta water, the products are dimethylcarbamide, methylamine, and mesoxalic acid.   C. F. B.

Tetrahydropapaverine. By GUIDO GOLDSCHMIEDT (*Monatsh.*, 1898, **19**, 321—332. Compare Abstr., 1888, 611).—Pope and Peachey (Trans., 1898, 893) have been able to decompose *r*-tetrahydropapaverine into its two optically active constituents by the aid of δ-bromocamphorsulphonic acid; the author had attempted the same resolution by the aid of tartaric acid, but without success. Even when an excess of tartaric acid is employed, the sparingly soluble normal tartrate, $(C_{20}H_{25}NO_4)_2C_4H_6O_6 + 17H_2O$, and not the acid tartrate, crystallises out. When dried at 105°, the salt still retains $1H_2O$, which it loses when heated at 155°.

When the base is crystallised from water or from very dilute alcohol, or when it is obtained by precipitating an aqueous solution of the hydrochloride with ammonia, it forms small, anhydrous needles, but when crystallised from dilute methylic alcohol, large prisms, $(C_{20}H_{25}NO_4)_2 + CH_4O$, are obtained, which lose their alcohol of crystallisation if heated or when left exposed to the air; when crystallised from absolute methylic alcohol, however, crystals without alcohol of crystallisation are obtained.

Tetrahydropapaverine nitrosamine, obtained by adding an excess of potassium nitrite to a solution of tetrahydropapaverine hydrochloride, crystallises from alcohol in well-developed, amber-coloured pyramids melting at 180—182°; it dissolves readily in acetone, chloroform

benzene, ethylic acetate, and warm alcohol, is only sparingly soluble in ether, and insoluble in light petroleum. When warmed with alcohol and hydrochloric acid, tetrahydropapaverine hydrochloride is obtained.

Tetrahydropapaveroline hydriodide, $C_{16}H_{17}NO_4,HI$, obtained when tetrahydropapaverine is heated for 4 hours with hydriodic acid (sp. gr. $= 1\cdot27$) and red phosphorus, crystallises in long, satiny needles containing $1\frac{1}{2}H_2O$. The *hydrochloride,* obtained by shaking an aqueous solution of the hydriodide with freshly precipitated silver chloride, crystallises with $2H_2O$.

Tetrahydropapaveroline is best obtained by dissolving the hydrochloride in water free from air, and decomposing with the requisite quantity of sodium hydrogen carbonate dissolved in water saturated with carbonic anhydride; it forms a slightly violet coloured, microcrystalline precipitate which is readily coloured by air or alkalis, is sparingly soluble in the usual organic solvents, turns brown at 200°, and melts and decomposes at about 255°. Aqueous solutions of the hydrochloride reduce Fehling's solution on boiling, and when treated with potassium and ammonium hydroxides turn violet. With ferric chloride, it gives the same reaction as catechol. J. J. S.

Derivatives of Cinchona Alkaloids. By WILHELM KOENIGS and MAX HÖPPNER (*Ber.,* 1898, **31**, 2355—2364. Compare Abstr., 1896, i, 264 and 328).—Deoxycinchonidine, mixed with methylic alcohol and methylic iodide and allowed to remain in darkness at ordinary temperatures for 24 hours, gives rise to a colourless, crystalline *methiodide,* $C_{19}H_{22}N_2,MeI$, which melts at 167—168°. When treated with alkalis, this compound undergoes the same change which Claus (Abstr., 1881, 289) has previously observed in the case of other alkylic haloids of cinchona bases.

When the methiodide, dissolved in very dilute sulphuric acid, is mixed with excess of caustic soda solution, and allowed to remain at ordinary temperatures, it is gradually transformed into *methyldeoxycinchonidine,* which crystallises from ether in colourless, feathery needles arranged in fan-like clusters, and melts at 64—65°. It is readily soluble in alcohol, ether, and benzene, and sparingly in light petroleum. A 10 per cent. alcoholic solution is feebly dextrorotatory, and a solution in dilute sulphuric acid has a blue fluorescence. The *mercurichloride* crystallises from dilute alcohol in needles, and the corresponding cadmium and zinc conpounds are crystalline and more soluble than those of deoxycinchonidine. The *platinochloride,* $C_{20}H_{24}N_2,H_2PtCl_6$, separates in reddish-yellow crystals, and blackens at 200° without melting.

When methyldeoxycinchonidine is heated with 20 per cent. aqueous phosphoric acid, it yields lepidine, but no base like apocinchenine is obtained on continued heating with concentrated hydrobromic acid. Oxidation of a cold solution of the base with permanganate in dilute sulphuric acid solution gives rise to chinchonic and n-methylcincholeuponic acids.

Further methylation of methyldeoxycinchonidine results in the formation of a *methiodide,* $C_{20}H_{24}N_2,MeI$, which crystallises from methylic

alcohol or water in white prisms and decomposes at 251°. The methiodide does not appear to yield a dimethyl base on treatment with alkalis.

Deoxycinchonine methiodide, $C_{19}H_{22}N_2$,MeI, prepared in a similar manner to deoxycinchonidine methiodide, crystallises from water in thick, colourless, tetragonal tablets and melts at 176°. On treatment with caustic soda, it yields a base which, like methyldeoxycinchonidine, melts at 64° and yields the above methiodide melting at 251°. Methyldeoxycinchonine and methyldeoxycinchonidine seem, therefore, to be identical. The deoxy-bases of quinine, conchinine, cinchonidine, and cinchonine are far more poisonous towards animals and infusoria than the corresponding parent substances.

When the hydrogen iodide additive product of cinchonine is heated for some time with aqueous phosphoric acid, a trace of formaldehyde is given off, and two bases which do not contain iodine are obtained. The one produced in larger quantity has properties resembling those of Lippmann and Fleissners' allocinchonine and also those of Hesse's apoisocinchonine; like the latter, it melts at 216°, whilst its sulphate and dihydriodide resemble those of the former; the platinochloride, $C_{19}H_{22}N_2O,H_2PtCl_6$, crystallises with $2H_2O$.

Cinchenine (cinchine), when heated on the water bath with excess of concentrated sulphuric acid, yields a crystalline sulpho-derivative insoluble in alkalis, to which the name of *sulphocinchine* [sulphocinchenine] is given, and which has the composition $C_{19}H_{20}N_2SO_3$; it crystallises from ethylic or methylic alcohol in colourless prisms, turns yellow at 150°, becomes red at 200°, decomposes at 280°, and is insoluble in water, ethylic acetate, and ether but dissolves readily in dilute acids, chloroform, and benzene.

Sulphocinchenine, when warmed for some time with dilute sulphuric acid or alcohol, is converted into an isomeride *cinchinesulphonic* [cincheninesulphonic] *acid* which is readily soluble in alkalis.

Chromic acid oxidises sulphocinchenine to cinchonic acid and a sulphonic acid the barium salt of which is soluble in water and alcohol; when heated with phosphoric acid at 170—180°, the base yields lepidine and an uncrystallisable sulphonic acid.

Dihydrocinchenine, which always accompanies cinchenine when the latter is prepared from commercial cinchonine, is not attacked by the sulphuric acid in the above reaction; it appears likely that the vinyl group, to which the SO_3 attaches itself in the case of cinchenine, is in dihydrocinchenine hydrogenised to an ethyl group.   G. T. M.

Salts of Hydrazoic Acid with some Organic Bases. By HERBERT POMMEREHNE (*Arch. Pharm.*, 1898, **236**, 479—486).—The hydrazoic acid employed was prepared by Dennstedt and Göhlich's (*Chem. Zeit.*, 1897, 21) method.

Strychnine hydrazoate, $C_{21}H_{22}N_2O_2$,$N_3H + H_2O$, prepared by dissolving the alkaloid in the acid, separates in beautiful, silken needles which, on exposure to air, lose a large portion of the acid, and this takes place completely on heating at 100°. The amount of hydrazoic acid in the salt was therefore estimated by titration with N/10 sodium hydroxide.

Brucine hydrazoate, $C_{23}H_{26}N_2O_4$,$N_3H + 3H_2O$, is a crystalline substance with similar properties; *quinine hydrazoate* crystallises in hard,

glistening, anhydrous plates; *codeine hydrazoate* crystallises in bunches of silken needles containing $2H_2O$. None of these salts explodes on drying.

Morphine does not form a salt with hydrazoic acid, nor do nicotine, coniine, pyridine, piperidine, quinoline, or tetrahydroquinoline.

A. W. C.

Periodides of Certain Alkaloids, and the Volumetric Estimation of Alkaloids as Higher Periodides. By ALBERT B. PRESCOTT and HARRY M. GORDIN (*J. Amer. Chem. Soc.*, 1898, **20**, 706—728).—On adding iodine dissolved in aqueous potassium iodide to a solution of a salt of an alkaloid, keeping the latter in excess throughout, the lowest periodide (generally a tri-iodide) is precipitated; if, however, the solution of the alkaloid is gradually added to the iodine solution, the highest periodide is generally formed exclusively. The periodides described below were all prepared as follows; a solution of the alkaloid (1 gram) in 200 c.c. of water acidified with hydrochloric or sulphuric acid, was gradually added to 500 c.c. of water containing 1 per cent. of free iodine and $1\frac{1}{2}$ per cent. of potassium iodide; after shaking until the solution became clear, the product was collected, and, when possible, recrystallised.

Atropine enneaiodide, $C_{17}H_{23}NO_3,HI,I_8$, prepared in this way, is a dark brown, almost black, powder, which dissolves only sparingly in ether, chloroform, benzene, or carbon bisulphide, but readily in hot alcohol; it separates from the latter unchanged in dark green prisms or leaflets, but is decomposed by hot water and by a concentrated solution of potassium iodide. When heated, it loses iodine at 90°, and melts at 140°. The additive iodine in the salt, and in those following, was determined by dissolving it in alcohol, adding an excess of standard sodium thiosulphate, and estimating the excess by means of standard iodine. The total iodine was determined by boiling the periodide suspended in water with zinc dust during 15 minutes, filtering, and estimating the iodine in solution, either gravimetrically or volumetrically, by means of silver nitrate. Quantitative experiments show that the hydriodic acid present in atropine periodide owes its origin to double decomposition taking place between the hydrochloric acid originally combined with the base and the potassium iodide present in the iodine solution. The enneaiodide is, however, also formed on adding atropine (20 grams) to a warm solution of iodine (30 grams) in chloroform (500 c.c.), but in this case the origin of the hydriodic acid is doubtful; if carbon bisulphide or tetrachloride is employed instead of chloroform, no periodide is formed.

On warming an alcoholic solution of atropine enneaiodide, or, better, atropine itself with the theoretical quantity of iodine, and an excess of mercury until the colour of the iodine is discharged, *monatropine hydriodide mercuric iodide,* $C_{17}H_{23}NO_3,HI,HgI_2$, separates in lustrous, yellow crystals, which melt at 80—90°, are sparingly soluble in ether and chloroform, but very soluble in warm alcohol. On treating an alcoholic solution of this compound with an excess of potassium iodide, the *salt,* $(C_{17}H_{23}NO_3)_2,2HI,HgI_2$, is formed; the latter crystallises in white, silky needles, melts at 98—99°, and is easily soluble in warm alcohol and water.

Strychnine heptiodide, $C_{21}H_{22}N_2O_2,HI,I_6$, is a dark brown powder which cannot be recrystallised, as it easily decomposes into iodine, and the tri-iodide ; *brucine heptiodide*, $C_{23}H_{26}N_2O_4,HI,I_6$, closely resembles it. The tetriodide, $C_{17}H_{19}NO_3,HI,I_3$, described by Jörgensen (*J. pr. Chem.*, 1870, [ii], **2**, 437), is the only periodide obtainable from morphine. *Aconitine heptiodide*, $C_{33}H_{45}NO_{12},HI,I_6$ (?), was prepared by adding aconitine to an excess of iodine dissolved in potassium iodide solution ; *aconitine tri-iodide*, $C_{33}H_{45}NO_{12},HI,I_2$ (?), prepared by adding a 1 per cent. solution of iodine to an acidified solution of aconitine, separates from alcohol in beautiful, brown-red crystals, melts at 211— 212°, and is sparingly soluble in ether, benzene, and chloroform.

The total iodine present in the periodides of brucine, morphine, and aconitine cannot be determined by the method given above ; the following has to be adopted. The periodide is left in contact during 30 minutes with zinc dust and concentrated aqueous ammonia, the latter expelled by heating, water added, and the mixture boiled during 10 minutes ; the liquid is filtered into a separating funnel, the residue of zinc washed with hot water until the solution has a volume of 200—300 c.c., and, when cold, the latter is rendered slightly acid with very dilute sulphuric acid. Twenty c.c. of carbon bisulphide and 10—12 drops of concentrated sulphuric acid saturated with nitrous acid are added, the iodine dissolved in the carbon bisulphide, transferred to a wetted filter, and the residue again extracted with carbon bisulphide. The iodine is washed on the filter, first with water, then with very dilute sodium hydrogen carbonate, and is transferred to a flask together with a 0·5 per cent. solution of the latter. Finally, the iodine is titrated with standard sodium thiosulphate.

The alkaloids dealt with can be determined volumetrically as follows. An acidified solution of the base is initially diluted by trial so that on adding 10—15 c.c. of it to 25—30 c.c. of decinormal iodine solution, making up to a known volume, and well shaking, the clear liquid obtained has a very dark red colour ; the iodine present in an aliquot portion of the latter is then determined. From the amount of iodine required to precipitate as periodide a known volume of the solution of the alkaloid, the concentration of the latter is determined by using the following factors, which give the ratio of alkaloid to iodine used in its precipitation : atropine, 0·2849 ; strychnine, 0·4390 ; brucine, 0·5179 ; morphine, 0·74918 ; and caffeine, 0·3834. The factors were verified in the first four cases by direct experiment.

Volumetric assay of opium.—One gram of finely powdered opium is triturated with 2—3 c.c. of a mixture containing 5 c.c. of concentrated aqueous ammonia, 5 c.c. of alcohol, 20 c.c. of ether, and 10 c.c. of chloroform, and the vessel covered and left during 3 hours ; 15 grams of finely powdered common salt is carefully mixed with the mass, the vessel left open during 3 hours at 30—35°, and subsequently exposed in a vacuum over solid paraffin until perfectly dry. The product is then extracted with benzene in a percolator, until, on evaporating a drop or two of the extract, dissolving in 4—5 drops of acidified water, and adding a solution of iodine in potassium iodide, no precipitate is obtained. The removal of alkaloids other than morphine is thus effected, and the morphine is extracted in the same

way by means of acetone (about 200 c.c.). After removing the latter by evaporation at a temperature not exceeding 40°, the residue is rubbed up with fresh lime-water, and the liquid, without filtering, is diluted to 100 c.c. After being vigorously shaken in a stoppered bottle during 30 minutes, the solution is filtered until exactly 50 c.c. has passed through, the filtrate is slightly acidified with hydrochloric acid, and 25 c.c. of decinormal iodine slowly added, keeping the vessel gently shaken. Water is added to a convenient volume, and the mixture shaken vigorously during about 20 minutes until, on standing, a perfectly clear, dark red liquid is obtained. Half the total volume is filtered, and the excess of iodine determined by the usual method. One gram of iodine = 0·74918 gram of morphine. W. A. D.

The Hyoscine-scopolamine Question. By LOUIS MERCK (*J. Soc. Chem. Ind.*, 1897, **16**, 515—516. Compare Schmidt, Abstr., 1897, i, 385).—E. Merck's "hyoscine," obtained from *Hyoscyamus*, consists entirely of scopolamine ; although very large quantities of solanaceous roots have been investigated in the Merck laboratories, no alkaloid, $C_{17}H_{23}NO_3$, corresponding with Ladenburg's hyoscine, could be obtained. Gadamer has, however, isolated a base, ψ-*hyoscyamine*, $C_{17}H_{23}NO_3$, from *Duboisia myoporoides*, which melts at 132—134° and is isomeric with atropine and hyoscyamine. The only other alkaloids present in *Duboisia myoporoides* are hyoscyamine, scopolamine, and considerable quantities of amorphous bases. Although it is often stated that hyoscine (that is, scopolamine) is present in the residual bases obtained in the manufacture of atropine, the investigation of large quantities of these has led the author to conclude that the statement is incorrect ; the scopolamine found by others is probably to be attributed to the roots used being imperfectly sorted. In discussing the identity of Hesse's atroscine with Schmidt's "inactive scopolamine," it is pointed out that, whereas the scopolamine hydrobromide obtained from *Hyoscyamus* always possesses normal rotatory power ($[a]_D = -24$—25°), that obtained from *Scopolia* roots shows a much lower optical activity ($[a]_D = -13·47°$). Since the conditions as regards alkali were identical in the two preparations, the author concludes that two chemically identical scopolamines which differ in optical activity, exist ready formed in *Scopolia*, whilst one only is present in *Hyoscyamus*. W. A. D.

Identity of Hesse's Atroscine and E. Schmidt's *i*-Scopolamine. By JOHANNES GADAMER (*Arch. Pharm.*, 1898, **236**, 382—392).—The author has definitely proved that atroscine (Hesse) and *i*-scopolamine (Schmidt) are the same alkaloid. Both can be prepared from scopolamine hydrobromide ($[a]_D = -13°$ 31′) by rendering alkaline with sodium carbonate and extracting with a mixture of chloroform and ether. If, after evaporation, the residue be rubbed with water and alcohol and then cooled, crystals of atroscine (Hesse) melting at 37—38° separate, but if a crystal of *i*-scopolamine (Schmidt) be added to the residue, compact, transparent crystals of the latter alkaloid melting at 56—56·5° are formed. Both substances are hydrates of the same alkaloid : atroscine contains $2H_2O$ and is the labile form, whilst scopolamine contains $1H_2O$ and is the stable form.

When a few drops of concentrated sodium hydroxide are added to scopolamine hydrobromide, the alkaloid is decomposed and sodium atropate is formed; more dilute caustic soda does not produce decomposition.

If atroscine (Hesse) is dissolved in alcohol, water added until a milkiness appears, and then a crystal of scopolamine, the latter alkaloid separates; and, conversely, atroscine can be converted into scopolamine when the amount of the labile form is three times as great as the dissolved stable form, and also when a freshly prepared solution of anhydrous i-scopolamine (Schmidt) is sown with a crystal of atroscine (Hesse).

The aurichlorides obtained from both alkaloids are identical, and melt at the same temperature, 208°.   A. W. C.

Bebeerine and Buxine. By MAX SCHOLTZ (*Arch. Pharm.* 1898, **236**, 530—541. Compare Abstr., 1896, i, 710).—The first part of the paper deals with some experiments which have already been noticed in this Journal (*loc. cit.*). Herzig and Meyer (Abstr., 1898, i, 53) have shown that bebeerine, both crystalline and amorphous, contains one methoxyl group and one methyl group attached to a nitrogen atom, and therefore the formula of the alkaloid is $OH \cdot C_{16}H_{14}O(OMe) \cdot NMe$.

When bebeerine is distilled with zinc dust, it yields orthocresol and methylamine; potassium permanganate and chromic acid decompose it completely; nitric acid gives rise to a yellow, amorphous powder, probably containing nitro-groups, which does not melt at 300°; potassium ferricyanide replaces two hydrogen atoms by one oxygen atom yielding the *substance* $C_{18}H_{19}NO_4$, which, after crystallisation from alcohol, decomposes without melting at 260°, and hydrogen peroxide produces a yellow mass partially soluble in glacial acetic acid. The soluble portion is an *acid*, $C_{18}H_{17}NO_7$, melting at 270°, and the insoluble portion an *aldehyde*, $C_{18}H_{17}NO_6$, crystallising in colourless needles and melting at 255°; its *phenylhydrazone* separates from alcohol in yellow needles melting at 166°.

Dibebeerine-xyleneammonium bromide, $C_6H_4(CH_2 \cdot NBr \cdot C_{18}H_{21}O_3)_2$, prepared by the action of orthoxylylenic bromide on the crystalline base dissolved in chloroform, forms colourless leaflets melting at 258°. It follows, therefore, that the nitrogen atom is not united to an aromatic residue, because aromatic tertiary amines do not combine with xylylenic bromide (Abstr., 1898, i, 565).

The author has been unable to crystallise buxine from methylic alcohol, and therefore considers that this alkaloid may not be identical with bebeerine (compare Flückiger, *Neues Jahrbuch der Pharm.*, **31**, 257).   A. W. C.

Alkaloids contained in Lycoris radiata Herb. By K. MORISHIMA (*Chem. Centr.*, 1898, i, 254—255; from *Arch. exp. Path. Pharm.*, **40**, 221—240).—From the alcoholic extract of the bulbs of *Lycoris radiata Herb.* (*Nerine japonica Miq.*) the author has isolated lycorine and sekisanine. *Lycorine*, $C_{32}H_{32}N_2O_8$, crystallises in large, colourless polyhedra, becomes yellow at 235°, and decomposes at 250°, is very slightly soluble in water, ether, alcohol, and chloroform, and easily so in acids. Its solutions give the reactions of alkaloids. In concen-

trated sulphuric acid, it forms a colourless solution which rapidly becomes yellowish-red, and in concentrated nitric acid a brownish-yellow solution ; with sodium molybdate and concentrated sulphuric acid, it gives a dirty green which turns blue, and with potassium permanganate and concentrated sulphuric acid a yellow coloration which passes through violet to yellow again. The *platinochloride* melts at 210° and the *hydrochloride*, $C_{32}H_{32}N_2O_8,2HCl+2H_2O$, crystallises in slender needles and melts at 208°. *Sekisanine*, $C_{34}H_{36}N_2O_9$, obtained from the alcoholic mother liquor of lycorine by means of ether, crystallises from dilute alcohol in long, colourless, four-sided prisms, melts at about 200°, is very slightly soluble in water, ether, chloroform and benzene, rather easily in alcohol, and easily in acids ; the solutions in concentrated sulphuric and nitric acids are yellow. It is precipitated by all the common reagents for alkaloids. With sodium molybdate and concentrated sulphuric acid, it gives a yellow, and with potassium permanganate and concentrated sulphuric acid a reddish, coloration, which turns violet and then yellow. The platinum salt melts at 194°.

Pharmacologically, lycorine belongs to the emetine group, acting as an emetic, then causing diarrhœa followed by paralysis.   E. W. W.

Hydrolysis of the Pectin of Gentian Root. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1898, [vi], 8, 49—52).— When the pectin extracted from gentian root by water at 110° (Abstr., 1898, i, 607) is oxidised by dilute nitric acid (sp. gr. = 1·15), mucic acid is obtained. When heated with 3 per cent. sulphuric acid for $1\frac{1}{2}$ hours at 110°, the pectin is hydrolysed, arabinose being formed ; the latter was identified by its melting point, crystalline form, and specific rotatory power. No other sugar could be detected.   W. A. D.

Action of Soluble Ferments on the Pectic Products of Gentian Root. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1898, [vi], 8, 145—150).—The soluble ferments produced during the growth of *Aspergillus niger* partially hydrolyse the pectose of gentian root, converting it into pectin. They have, however, no action on pectin prepared from gentian by digesting the latter with water at 110° (Abstr., 1898, i, 607). Although pectin obtained in this way is not changed by saliva or by emulsin, it is converted into a substance possessing cupric-reducing power by diastase precipitated from malt extract by alcohol. From this, the author concludes that malt-diastase consists of at least three enzymes ; an *amylase*, capable of hydrolysing starch, a *trehalase* which hydrolyses trehalose, and an *enzyme* which effects hydrolysis of the pectin of gentian root.   W. A. D.

Presence in Malt of a Soluble Ferment Acting on Pectin. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1898, 127, 191—194. Compare preceding abstracts).—Powdered gentian root was extracted with boiling 80 per cent. alcohol and then heated with water at 110° in an autoclave. The solution of pectin thus obtained is readily acted on by diastase at the ordinary temperature, the action being much facilitated by the addition of a little chalk, which serves the

purpose of neutralising the slight acidity of the pectin. After 48 hours, the liquid is found to have acquired reducing properties and is no longer coagulated by pectase, whilst the addition of two volumes of 95 per cent. alcohol only produces a small, pulverulent precipitate. Neither the amylase of saliva nor the ferments (trehalase, &c.) of *Aspergillus* have any action on pectin, and hence it is inferred that the diastase of malt contains a special ferment, other than amylase or trehalase, capable of acting on the pectin of gentian. N. L.

Proteolytic Enzyme of Yeast Extract. By L. GERET and MARTIN HAHN. (*Ber.*, 1898, 31, 2335—2344. Compare Abstr., 1898, ii, 245 and 246).—This enzyme is not only capable of decomposing the albumin present in the yeast extract, but also attacks additional quantities of albumin from other sources. When 20 c.c. of a solution of egg-albumin, containing 3·5 per cent. of coagulable albumin, is allowed to digest for 6 days with 20 c.c. of yeast extract containing 5·2 per cent. of albumin, it is found that, not only is the whole of the latter rendered soluble, but also 21 per cent. of the added albumin. If a sample of yeast extract be coagulated after one hour's digestion, the filtrate is found to contain leucine and tyrosine, and traces of albumoses, but no peptone.

Yeast extract to which 2 per cent. of peptone or albumose is added, gives at first a marked biuret reaction, but after digestion for 3 days this is no longer obtained. The total nitrogen in the digested extract is determined, and the amount present in organic bases is obtained by precipitating these with phosphotungstic acid, the difference giving the amount present in the form of amido-acids. A table is given showing the change in these quantities after definite intervals of time ; as the digestion is prolonged, the amount of basic nitrogen reaches a maximum and then decreases, so that after two weeks the ratio of basic to amido-acidic nitrogen is the same as at the commencement of the experiment.

When air is passed through yeast extract for a given time, it is found that the amount of coagulated albumin is less than when hydrogen is passed through it.

The amount of hypoxanthine precipitable by ammoniacal silver solution without previous boiling with dilute sulphuric acid increases with the time of digestion. Agitation of the yeast extract, either by shaking in a vacuum or by passing air or hydrogen through the mixture, favours the formation of this precipitable hypoxanthine. There is still in the extract a further quantity of hypoxanthine which is only precipitated by ammoniacal silver after boiling with dilute sulphuric acid. The amount of this "latent form" of hypoxanthine is not altered by mechanical agitation.

The amount of phosphorus as phosphoric acid in the extract is determined in the usual way after removing the albumin by mercuric chloride and hydrochloric acid ; it is found to increase with the time of digestion. After 1 hour, two-thirds of the total phosphorus is present as phosphoric acid, and after 9 days one-fifth still remains combined with organic compounds. The total quantity of sulphur is inconsiderable ; and only a small proportion of this is converted into

sulphuric acid; the amount separating in this form increases slightly with the time.

The activity of the proteolytic enzyme of yeast is diminished, but not destroyed, by 1 per cent. hydrocyanic acid, and it recovers its original strength if the acid be again removed.

Tables are also given indicating the presence of proteolytic enzymes in extracts from *Sarcina rosea* and tuberculosis and typhus bacilli.

The formation of these enzymes in animal and vegetable cells appears to be more common than is generally supposed; it remains to be decided whether the enzyme is excreted by the individual cell or whether it is retained in the cell-contents and only rendered manifest when the cell undergoes disruption. G. T. M.

Taka-diastase. By WINTHROP E. STONE and H. E. WRIGHT (*J. Amer. Chem. Soc.*, 1898, **20**, 639—647).—The authors have compared the action of taka-diastase on potato starch with that of diastase precipitated from malt extract by alcohol. The iodine test for starch shows that the latter is acted on more rapidly, at the outset, by taka-diastase than by malt-diastase; in the former case, an almost immediate change from the typical blue of the starch-iodine compound to reddish and violet tints takes place, whereas in the latter a longer time elapses before this occurs. The complete conversion, however, of starch into forms which no longer give colour reactions with iodine is effected much more rapidly by malt-diastase than by taka-diastase. The specific rotatory powers of the conversion products of starch by malt- and taka-diastase indicate that, under the same conditions, the latter effects a more rapid transformation to maltose than the former, and this result was confirmed by determining in each case the actual amount of maltose formed.

Owing to the incomplete conversion of starch into maltose by taka-diastase, the latter cannot be used as a substitute for malt-diastase in determining starch in vegetable materials; thus a sample of wheat which was found to contain 55·46 per cent. of starch by using malt extract, appeared to contain only 52·94 per cent. when taka-diastase was employed. W. A. D.

A Product of the Decomposition of Albumin. By JACQUES M. ALBAHARY (*Compt. rend.*, 1898, **127**, 121—124).—When dry egg-albumin is mixed with water and amorphous phosphorus, and iodine is gradually added, a reaction takes place with development of heat, and after some time a white precipitate separates on the surface of a yellow liquid. This precipitate contains no iodine and leaves no ash when burnt; it consists solely of carbon, hydrogen, nitrogen, oxygen, and sulphur. When dried at 110°, it becomes reddish-brown, hard, brittle, and transparent, melts and decomposes at 260—270°, is almost insoluble in water and solutions of normal alkali carbonates, and also in solutions of sodium phosphate or sodium chloride. It dissolves, however, in presence of alkali hydroxides, especially ammonia, and is reprecipitated by dilute acids, but dissolves in strong organic acids. With sodium hydroxide, it yields a salt which crystallises from aqueous alcohol in long needles, and begins to decompose at 250° but does not melt at 270°. It also forms, in presence of hydrochloric acid, a picrate,

a gold salt, and a platinum salt, the first two being readily crystallisable. The molecular weight of the gold salt is 2011 and of the nitrogen compound 1670. The author calls the compound *ovalbuminic acid* ; it contains C, 50·05 ; H, 7·04 ; N, 17·20 ; S, 2·14 ; O, 23·54.

When a solution of the sodium salt is dialysed, it yields an almost neutral liquid in which calcium salts produce a white precipitate and which is coagulated by a mixture of sodium chloride with calcium or magnesium sulphate, although sodium chloride alone has no effect.

The acid gives the xanthoproteic, biuret, Molisch, Millon and Adamkiewicz reactions, and is reprecipitated from its hydrochloric acid solution by phosphomolybdic and phosphotungstic acids and by Bouchardat's reagent. Its acetic acid solution gives, with potassium ferrocyanide, a greenish precipitate, which, when heated with a trace of hydrochloric acid, becomes deep blue. Its hydrochloric acid solution gives a blue coloration only with the ferrocyanide. C. H. B.

Products of the Trypsin Fermentation of Casein. By FRANZ RÖHMANN (*Ber.*, 1898, **31**, 2188. Compare Abstr., 1898, i, 56).—By warming the crude leucine (*loc. cit.*) with phenylthiocarbimide, potassium hydroxide, and a little dilute alcohol, the leucine can be separated in the form of the phenylthiohydantoic acid, which changes, when kept, into the phenylhydantoin, $C_4H_9 \cdot CH \begin{smallmatrix} CO \cdot NPh \\ | \\ NH \cdot CS \end{smallmatrix}$, melting at 178° (Aschan, Abstr., 1883, 1107 ; 1884, 907).

C. F. B

Organic Chemistry.

Action of Bromine on Propylic Bromide in presence of Aluminium Bromide. By A. MOUNEYRAT (*Compt. rend.*, 1898, 127, 273—276).—The author has applied to propylic bromide the method already used in the case of ethylic bromide (this vol., i, 1). One hundred grams of the substance to be brominated was heated with 20 grams of aluminium bromide and the calculated quantity of bromine. In this way, he has readily prepared propylenic bromide,
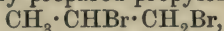
$$CH_3 \cdot CHBr \cdot CH_2Br,$$

from propylic bromide, and tribromopropane, $CH_3 \cdot CHBr \cdot CHBr_2$, from the propylenic bromide. In the formation of the tribromopropane, which is accompanied by small quantities of its isomeride, $CH_2Br \cdot CHBr \cdot CH_2Br$, and a tetrabromopropane, it is probable that the propylene bromide loses hydrogen bromide, and is converted into bromopropylene, which at once combines with bromine, or possibly with hydrogen bromide.

Tetrabromopropane, $CH_2Br \cdot CHBr \cdot CHBr_2$, is obtained in a similar way from either of the derivatives $CH_3 \cdot CHBr \cdot CHBr_2$, or

$$CH_2Br \cdot CHBr \cdot CH_2Br,$$
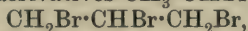
and, in its turn, yields pentabromopropane, $CHBr_2 \cdot CHBr \cdot CHBr_2$.

C. H. B.

Action of Acetylene on Mercuric Nitrate. By KARL A HOFMANN (*Ber.*, 1898, 31, 2783—2787. Compare Abstr., 1898, i, 635).—H. Erdmann and Köthner (this vol., i, 21) describe a substance obtained by the action of acetylene on a hot solution of mercuric nitrate as a double compound of mercurous carbide and nitrate, $HgC:CHg, Hg NO_3 + H_2O$. It is not an acetylide, however, for it gives no acetylene when heated with hydrochloric acid, but aldehyde instead. Neither is it a mercurous compound, for, when it is digested for $\frac{1}{4}$ hour with dilute hydrochloric acid, 83·8 per cent. of mercuric chloride is formed, but only 2·3 per cent. of mercurous chloride, and this, no doubt, on account of the reducing action of the aldehyde simultaneously formed; further, potassium cyanide solution dissolves the compound without deposition of mercury, and ammonia produces no black coloration. The substance analysed by Erdmann and Köthner contained a little mercury; after removal of this by digestion with dilute nitric acid, the analytical numbers agree with the formula $NO_3 \cdot Hg \cdot C(:Hg_2:O) \cdot CHO$, that of a substituted aldehyde.

The compound is best prepared by dissolving yellow mercuric oxide (20 grams) in dilute nitric acid (70 c.c. of 30 per cent. acid and 500 c.c. of water), filtering, and passing a fairly rapid current of acetylene for 2 hours through the solution at a temperature of 18°. The precipitate is then collected, digested three times with 8 per cent. nitric acid (150 c.c.) at the ordinary temperature for 6 hours, filtered, washed with alcohol and ether, and dried under diminished pressure over sulphuric acid.

C. F. B.

Acetylene Tetrabromide and Tribromethylene. By KARL
ELBS and J. NEWMANN (*J. pr. Chem.*, 1898, [ii], **58**, 245—254).—In
preparing acetylene tetrabromide from acetylene generated from
calcium carbide, the gas is best purified from hydrogen phosphide by
passing it through a solution of mercuric chloride acidified with hydro-
chloric acid. The pure tetrabromide is an almost colourless liquid
boiling at 124—126° under a pressure of 15 mm. When reduced with
zinc dust and acetic acid, or zinc dust and sodium ethoxide in alcoholic
solution, the principal products are acetylene dibromide and tri-
bromethylene, and small amounts of ethylene dibromide. Aluminium
amalgam reduces the tetrabromide so rapidly and completely to ace-
tylene dibromide that it may be used as a means of preparing that
substance.

Attempts to replace bromine in acetylene tetrabromide by iodine or
acetyl groups proved unsuccessful; the action of aniline, dimethyl-
aniline, or alcoholic ammonia causes the production of tribromethylene.

When the tetrabromide is heated with bromine and aluminium in
sealed tubes at 90—95°, hexabromethane is produced.

Bromine acts readily on tribromethylene, producing pentabrom-
ethylene; iodine reacts but slightly, whilst chlorine gives rise to
chlorotribromethylene, crystallising in colourless needles melting at
35° (compare Denzel, Abstr., 1880, 228), and uniting with bromine to
form chloropentabromethane melting at 170°.

Zinc dust acts on tribromethylene, producing acetylene; concen-
trated sulphuric acid gives rise to pentabromethane; fuming sulphuric
acid decomposes the substance completely; and nitrous anhydride
produces *tribromonitroethylene* as a heavy, pale yellow liquid, with
penetrating odour, boiling at 108—110° at 21 mm. (compare Scholl
and Brenneisen, Abstr., 1898, i, 345).

Chlorine acts on pentabromethane at 200—205°, with production of
chlorotribromethylene, whilst antimony pentachloride gives rise to
hexachlorethane.   A. W. C.

**Hydrocarbon, C_3H_4, a Secondary Product of the Decompo-
sition of Barium Pyromucate.** By PAUL FREUNDLER (*Bull. Soc.
Chim.*, 1897, [iii], **17**, 614—616).—The hydrocarbon, C_3H_4, obtained
when barium pyromucate is distilled (see this vol., i, 120), has a some-
what aliaceous odour, and precipitates an alcoholic solution of mercuric
chloride, but not ammoniacal cuprous chloride or silver nitrate.
When treated with bromine, it yields a small quantity of a *dibromide*
boiling at about 50° under reduced pressure, but the chief product is
a *tetrabromide*, $C_3H_4Br_4$, a liquid boiling at 162° at 20 mm. pressure.
This compound has not been obtained pure, as it is extremely
hygroscopic, and as it is not identical with allylene tetrabromide,
it is probable that the hydrocarbon has the constitution $CH_2{<}{CH \atop CH}$.

                                                                    J. J. S.

**Action of Ammonia on Zinc and Mercuric Cyanides, and
on Haloid Double Salts of the Latter.** By RAOUL VARET (*Ann.
Chim. Phys.*, 1897, [vii], **10**, 5—18. Compare Abstr., 1896, i, 3,
633, ii, 88, 149, 512; 1897, i, 585, ii, 38, 99).—The *compound*

$Zn(CN)_2,2NH_3,H_2O$, obtained in transparent, prismatic crystals is produced by the action of ammonia on aqueous solutions of zinc cyanide; the *compound* $Zn(CN)_2,2NH_3$, is formed in alcoholic ammoniacal solutions, or by the action of dry ammonia on the heated cyanide. Both these substances are very soluble in aqueous and alcoholic ammoniacal solutions, and rapidly decompose on exposure to the air.

The *compound* $2Hg(CN)_2,4NH_3,H_2O$ separates in white, prismatic needles when a saturated solution of mercuric cyanide in concentrated ammonia is cooled in a freezing mixture; the *compound* $2Hg(CN)_2,2NH_3,H_2O$ is obtained when a saturated solution of mercuric cyanide in less concentrated ammonia is allowed to crystallise at $0°$; both substances are very unstable, and are completely resolved into their constituents when heated to 100°. The *compound* $Hg(CN)_2,2NH_3$ results from the employment of alcoholic solutions; it separates in transparent, prismatic needles, which decompose rapidly on exposure to air. The *compound* $Hg(CN)_2,NH_3$, produced in an aqueous ammoniacal solution of mercuric cyanide in the presence of excess of the salt, separates from the filtrate in hard, granular crystals; it is more stable than the preceding compounds, but is completely decomposed on heating at 100°. No definite compound results from the action of dry, gaseous ammonia on warm mercuric cyanide. The double salt, $Hg(CN)_2,HgCl_2$, when treated with alcoholic ammonia, is resolved into its components; mercuric chloride gives rise to an insoluble *compound*, $2HgCl_2,3NH_3$, whilst mercuric cyanide yields the substance $Hg(CN)_2,2NH_3$. A greyish-white *substance*, $2Hg_2(CN)_2Cl_2,3NH_3$, is obtained by the action of dry ammonia on gently heated mercuric chlorocyanide. The chlorocyanide, when treated with aqueous ammonia, gives a precipitate of mercuric ammonium chloride, NH_2HgCl; if zinc cyanide be added to the mixture, the precipitate redissolves, and on concentrating the solution the *double* salt, $2Hg(CN)_2,ZnCl_2,4NH_3$, is obtained in nodular crystals; this compound is also produced by the action of aqueous ammonia on the double salt, $2Hg(CN)_2,ZnCl_2,7H_2O$.

The latter method is employed in preparing the following series of analogously constituted *double* salts. $2Hg(CN)_2,ZnBr_2,4NH_3$; $2Hg(CN)_2,CuCl_2,4NH_3$; $2Hg(CN)_2,CuBr_2,4NH_3$;

$$2Hg(CN)_2,CdBr_2,4NH_3,2H_2O;$$

$2Hg(CN)_2,CdBr_2,4NH_3$; $2Hg(CN)_2,CdI_2,4NH_3$. These compounds are crystalline, and the copper and cadmium derivatives do not evolve ammonia when heated to 100°. G. T. M.

Action of Chlorine on Secondary Alcohols. By ANDRÉ BROCHET (*Ann. Chim. Phys.*, 1897, [vii], 10, 134—144).—This paper gives a detailed account of the ultimate action of chlorine on isopropylic alcohol and methylhexylcarbinol; the results obtained have already been published (see Abstr., 1895, i, 259; 1897, i, 4).

G. T. M.

Action of Chlorine on Primary Alcohols. By ANDRÉ BROCHET (*Ann. Chim. Phys.*, 1897, [vii], 10, 289—380).—This paper contains a very detailed account of work which has already been published. The theory of the chlorination of ethylic alcohol is fully discussed, and the work of previous investigators compared with the results

obtained by the author with other primary alcohols. The action of chlorine on methylic alcohol (Abstr., 1895, i, 637, and 1896, i, 276), on propylic alcohol (Abstr., 1896, i, 114), and on isobutylic alcohol (Abstr., 1892, 1292 ; 1894, i, 484 ; and 1897, i, 3, 4) has already been made known.

The author puts forward the following generalisation. When chlorine acts on any primary alcohol, except methylic alcohol, the first product of reaction is a dichloro-derivative, $C_nH_{2n}Cl\cdot CHCl\cdot OH$; this either passes into a monochloraldehyde, $C_nH_{2n}Cl\cdot COH$, by loss of hydrogen chloride, or condenses with another molecule of alcohol to form an unsymmetrical dichloroxide, $C_nH_{2n}Cl\cdot CHCl\cdot O\cdot CH_2\cdot C_nH_{2n+1}$. This statement has been verified in the case of ethylic, propylic, isobutylic, and isoamylic alcohols (Abstr., 1898, i, 549). In the case of methylic alcohol, the initial product is chloromethylic alcohol, which, by elimination of water, is converted into symmetrical dichloromethylic oxide.   G. T. M.

Action of Chlorine on Tertiary Amylic Alcohol. By ANDRÉ BROCHET (Ann. Phys. Chim., 1897, [vii], 10, 381—387).—Chlorine has no action on cold dimethylethylcarbinol in diffused daylight, but at the boiling point of the alcohol, it is rapidly absorbed without evolution of gas. The products of the reaction are fractionated ; the lowest fraction contains tertiary amylic chloride (2-methyl-2-chlorobutane), $CMe_2Cl\cdot CH_2Me$, and chloramylene (2-methyl-3-chlorobutene), $CMe_2:CMeCl$. This mixture is treated with bromine and subsequently steam distilled, when amylic chloride is obtained in the distillate and chloramylene dibromide remains in the residue.

The higher fractions contain some unattacked alcohol and higher chlorinated derivatives of isopentane (2-methylbutane), dichlorisopentane, $CMe_2Cl\cdot CHMeCl$, and trichlorisopentane, have been isolated. The latter boils at 176°, its sp. gr. $= 1\cdot215$ at 15°/4°, and its index of refraction $n_D = 1\cdot472$ at 21°.

The chief product of the action of chlorine on the cold alcohol in the presence of sunlight is the above-mentioned dichlorisopentane. When the gas is passed into a boiling mixture of the alcohol and water, the chief product is trichlorisopentane ; chloro-derivatives of higher boiling point, acetone, acetic, formic, and carbonic acids are also formed, but no amylic chloride could be detected. The first action of chlorine results in the formation of $CMe_2Cl\cdot CHMeCl$, this substance loses hydrogen chloride and forms $CMe_2:CMeCl$, addition of chlorine to the chloramylene produces $CMe_2Cl\cdot CMeCl_2$; the amylic chloride is produced by a secondary reaction between the hydrochloric acid liberated and the unattacked alcohol.   G. T. M.

Dextro-licarhodol. By PHILIPPE BARBIER and GEORGES LÉSER (Bull. Soc. Chim., 1897, [iii], 17, 590—596).—When pure licareol (boiling at 86—88° under 10 mm. pressure) is heated with its own weight of acetic anhydride during 8 hours at 150—160° and the product rectified under a pressure of 10 mm., three fractions are obtained. The first passes over between 50° and 80°, and consists mainly of terpenes ; the second, passing over between 80° and 105°, consists mainly of unaltered licareol, and the third, boiling at 105—130°, when further fractionated with the aid of a dephlegmator,

yields a colourless liquid boiling at 119—120° under 10 mm. pressure; this has the composition $C_{10}H_{17} \cdot OAc$. The higher fractions contain an ether, $(C_{10}H_{17})_2O$, boiling at 145—150° under 10 mm. pressure. The acetate is hydrolysed when the theoretical quantity of alcoholic potash is run in at the ordinary temperature, and the mixture then heated to 100° for an hour. The alcohol, $C_{10}H_{18}O$, licarhodol, thus obtained boils at 112—114° under 9 mm. pressure, has an agreeable odour, sp. gr. at $0° = 0.904$, and rotatory power $[a]_D = +4°8'$. The yield is about 800 grams from 5 kilos. of licareol. When oxidised with permanganate, licarhodol gives dimethyl ketone, terebic acid melting at 174°, and levulinic acid. When oxidised with chromic mixture, the products are methylheptenone, $CMe_2 \colon CH \cdot CH_2 \cdot CH_2Ac$, a small quantity of geranial-citral, and an acid, $C_9H_{14}O_3$, probably methylheptenonecarboxylic acid.

The following is the constitution suggested for licarhohol,

$$CH_2 \colon CMe \cdot CH(CH_2OH) \cdot CH_2 \cdot CH \colon CMe_2. \qquad \text{J. J. S.}$$
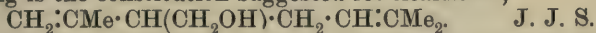
Action of Neutral Salts on Glucose at a Higher Temperature. By H. C. PRINSEN GEERLIGS (*Chem. Centr.*, 1898, i, 712; from *Arch. Javasuikerindustrie*, 1898).— The author finds that, not only do the salts of weak organic acids bring about the inversion of sugar in presence of glucose, but that at 100° they also act on the glucose, converting the dextrose into levulose, or when the latter is in excess, inversely converting it into dextrose; the same change is effected by the alkali salts of strong mineral acids (see following abstract), but to a very much smaller extent. The amount of change is proportional to the time during which the action has proceeded and to the concentration of the solution of the salt. A portion of the glucose is converted into organic acids, and it is these acids which sometimes interfere with Romijn's test for dextrose with iodine solution containing borax (*Arch. Suikerindustrie*, 1897, 1001) by absorbing iodine and forming iodoform. The feeble rotatory power of molasses containing much invert-sugar is due to the fact that the raw sugar molasses contain considerable quantities of salts of organic acids. E. W. W.

Inversion of [Cane] Sugar by Neutral Salts in Presence of Glucose. By H. C. PRINSEN GEERLIGS (*Chem. Centr.*, 1898, i, 711; from *Arch. Suikerindustrie*, 1898).—The quantity of sucrose inverted by neutral salts in presence of glucose (see *Arch. Suikerindustrie*, 1895) is approximately proportional to the time during which the action takes place and to the amount of glucose originally present; the quantity of salt (sodium chloride) has only a very slight influence on the action. The action of the glucose is due to the liberation of a very small quantity of acid by the formation of a glucosate of the base, but when calcium carbonate or a salt of a weak organic acid is added, the inversion is retarded or prevented. The more easily dissociated salts are the more active, thus magnesium chloride and the chlorides of the alkaline earths are more effective than the chlorides of the alkalis. The acids contained in the salts also have a great influence; the following salts of potassium are arranged in order of decreasing activity : chloride, bromide, nitrate, sulphate,

chlorate, oxalate, and succinate. Since the monosaccharides, dextrose, levulose, galactose, and lactose act like glucose, whilst the alcohols and the di- and tri-saccharides are inactive, the presence of an aldehyde group may be necessary to bring about the reaction.

<div align="right">E. W. W.</div>

Inversion of Saccharose by Water. By BOHUSLAV RAÝMAN and OTTOKAR ŠULC (*Chem. Centr.*, 1898, i, 608—609 ; from *Zeit. Zuck.-Ind. Böhm.*, 22, 233—248. Compare Abstr., 1898, i, 348).—Saccharose is inverted by water at temperatures above 110°, but when acid is added the change takes place at a lower temperature. When extremely pure water is used, 10 per cent. and weaker solutions of saccharose are not affected by boiling for some hours, but when the water has a considerable conductivity, the action commences ; generally speaking, the more concentrated the solution is after boiling, the more quickly inversion begins. When platinum vessels are used, the action occurs more rapidly, no matter how small the conductivity of the water, and in vessels of other metals inversion takes place with varying rapidity. The action of the metals of the platinum group in powder was investigated ; of these, palladium induced the most rapid change, iridium alone retarded the action, and in many cases a faint acidity of the solution could be detected by Congo-red. When metallic vessels were used, this acidity was only apparent in the cases of copper and silver. The author ascribes the influence of metals partly to a hydrolytic action and partly to the formation of acids from the sugar ; like acids, the metals are supposed to increase the chemical activity or "ionisation" of the water. The acid compounds are formed by a process of migration of the oxygen atoms analogous to certain reactions of sugars with alkalis and water. The oxidation of hydroxy-aldehydes and hydroxy-ketones is explained by a process of successive dehydration and hydration, whereby the groups $CH_2 \cdot OH$ and $CH \cdot OH$ become CH_3 and CH_2 respectively, and the terminal carbon atoms either form carboxyl groups, formic acid, or carbonic anhydride. At the same temperature, increase of pressure diminishes the inversion effected.

<div align="right">E. W. W.</div>

Hydrolysis of Polysaccharides by Yeast Enzymes. By ANUSCHAWAN KALANTHAR (*Zeit. physiol. Chem.*, 1898, 26, 88—101).—The author has studied the hydrolytic action of yeasts from various wines and beers, and from the Russian beverage "kissly-schtschi" and the Armenian beverage "mazun" on the polysaccharides. Pure cultures were prepared in each case, and both fresh and dried cells and aqueous extracts were employed. The polysaccharides experimented on were cane-sugar, maltose, lactose, melibiose, trehalose, melitriose (raffinose), melicitose, and α-methylglucoside ; 10 per cent. solutions were submitted to the action of the yeast, a little toluene being added to prevent alcoholic fermentation. The amount of monosaccharide produced was determined either by titration with Fehling's solution, or in the case of those polysaccharides which themselves reduce Fehling's solution, by ascertaining the amount of osazone produced with phenylhydrazine ; the results

obtained are tabulated, and they indicate that the dried yeast and the aqueous extract possess a greater hydrolytic action than the fresh cells. Cane-sugar and raffinose were readily hydrolysed by all the forms of yeast employed. Maltose and α-methylglucoside were usually decomposed to the same extent, but in one or two cases the latter compound appeared to be more readily attacked. Although melibiose and lactose are formed from the same components (d-glucose and d-galactose), they behave somewhat differently towards enzymes; the amount of the former hydrolysed varied with the temperature, only one wine yeast being capable of hydrolysing it at 25°, but in every case negative results were obtained with lactose.

Trehalose was hydrolysed by all the yeasts in the dried condition (compare Abstr., 1895, i, 441), except in the case of an orange-red yeast from "mazun"; fresh wine or distillery yeast also induced appreciable hydrolysis. Melicitose was hydrolysed by all the beer yeasts, with one exception.

The author adds a description of the preparation of "mazun" from milk. This beverage contains, besides bacilli and micrococci, nine species of yeast cells; seven of these have been isolated by Lindner and the author, and a table showing their hydrolytic action on maltose, α-methylglucoside, trehalose, lactose, and cane-sugar is included in the paper. G. T. M.

Formation of Furfuraldehyde from Starch and its Derivatives. By FAUSTO SESTINI (*L'Orosi*, 1898, 21, 109—113).— Furfuraldehyde, to which the odour of new bread is partly due, is produced by the simple heating of all varieties of bread, the crumb requiring to be heated to 140—160°, whilst for the crust, which has been already more strongly heated in the cooking, a temperature of 110—115° is sufficient. The aldehyde does not exist ready formed in the bread, since none is obtained from it by steam distillation, and its production must be attributed to the decomposition of pentoses derived from the bran, or to that of the starch and allied carbohydrates. Dry starch of various kinds was found to yield furfuraldehyde when heated to 180° and upwards, whilst if previously moistened with a minute quantity of sulphuric or hydrochloric acid, even a temperature of 100° was sufficient for its production. Nageli's "starch granulose," deprived of every trace of free acid, evolves furfuraldehyde at 100° or a few degrees higher, and the different varieties of dextrin behave in a similar manner. Furfuraldehyde may be obtained from pentoses without the aid of acids, as various kinds of gum were found to yield this substance when heated in the dry state to 180—200°, and also, if slightly moistened with water, at 120°. Two specimens of purified rice starch, when distilled with hydrochloric acid of sp. gr. = 1·06, yielded respectively 1·16 and 0·44 per cent. of furfuraldehyde, quantities far greater than could be derived from traces of pentoses possibly present in the starch and which, moreover, could not be detected therein. It follows from these results that the amount of furfuraldehyde obtainable from starch and allied carbohydrates is by no means a neglige-

able quantity, and this fact must be taken into account in estimating pentoses by the furfuraldehyde method.   N. L.

Derivatives of Bromethylamine and Bromopropylamine. By SIEGMUND GABRIEL and ERNST LEUPOLD (*Ber.*, 1898, **31**, 2832—2839). —*Orthohydroxybenzylidenebromethylamine*, $OH \cdot C_6H_4 \cdot CH:N \cdot C_2H_4Br$, formed by the condensation of bromethylamine hydrobromide with salicylaldehyde in presence of an alkali, crystallises in yellow needles, melting at 56—57°.

Ethylenepseudothiocarbamide is converted by nitrous acid into μ-phenylthiazoline, $\begin{array}{c} CH_2 \cdot S \\ CH_2 \cdot N \end{array}\!\!>\!\!CPh$; the picrate crystallises in lemon-yellow needles, which soften at 165° and melt at 173—174°, whilst the dichromate, $(C_9H_9NS)_2,H_2Cr_2O_7$, forms orange-yellow needles. The formation of this compound favours the supposition that ethylenepseudothiocarbamide contains an amido-group, and has the constitution $\begin{array}{c} CH_2 \cdot S \\ CH_2 \cdot N \end{array}\!\!>\!\!C \cdot NH_2$. The thiazoline derivative is accompanied by a substance crystallising in flat, yellowish needles which melt and decompose at 203—204°. This compound is probably *nitroethylenepseudothiocarbamide*, but has not been obtained in sufficient quantity for further examination.

μ-Phenyl-β-methylthiazoline, $\begin{array}{c} CHMe \cdot S \\ CH_2 \longrightarrow N \end{array}\!\!>\!\!CPh$, is obtained from propylenepseudothiocarbamide, and is identical with that previously obtained from thiobenzamide (Gabriel and von Hirsch, Abstr., 1897, i, 120). *Nitropropylenepseudothiocarbamide*, $C_4H_7NS \cdot NO_2$, crystallises in flat, oblique needles, which melt and decompose at 166°.

Mercaptothiazoline is decomposed by hydrochloric acid at 155° with formation of amidomercaptan. Mercaptomethylthiazoline, when treated in a similar manner, yields *amidopropyl-β-mercaptan hydrochloride*, $SH \cdot CHMe \cdot CH_2 \cdot NH_2,HCl$, which crystallises in microscopic tablets and melts at 87—88°; the *picrate* crystallises in compact, rhombic tablets melting at 143—144°; on treatment with iodine, it yields *diamidopropylic β-bisulphide*, the hydrochloride of which, $C_6H_{16}S_2N_2,2HCl$, melts at 213—214°, the *picrate* forms short, thick prisms melting at 162—163°.   A. H.

Chemical Activity of Organic Ammonium Salts. By WOLFGANG BRENDLER and JULIUS TAFEL (*Ber.*, 1898, **31**, 2683—2686. Compare Tafel, Abstr., 1898, i, 471).—*Trimethylacetonylammonium bromide*, $COMe \cdot CH_2 \cdot NMe_3Br$, obtained on passing trimethylamine into an ethereal solution of bromacetone, crystallises in well-formed, colourless needles when the alcoholic solution is exposed to an atmosphere of ether; it melts at 190°, and at 195° gives rise to a yellow distillate and tetramethylammonium bromide. The *phenylhydrazone* is a crystalline substance which dissolves more readily in water than in alcohol; Fehling's solution precipitates a yellow oil which is volatile in steam.

Bromacetonyltrimethylammonium bromide, $C_6H_{13}NOBr_2$, obtained by the action of bromine on trimethylacetonylammonium bromide,

crystallises from alcohol. If bromine water is employed instead of the undiluted halogen, a reddish-yellow, crystalline precipitate is formed having the properties of an ammonium tribromide; when an attempt is made to dry this substance, hydrogen bromide is eliminated, and bromacetonyltrimethylammonium bromide is formed. The aqueous solution of the last-named substance yields trimethylamine when heated. M. O. F.

Propylnitramine and its Alkyl Derivatives, and the Probable Existence of a New Class of Neutral Nitramines. By HERM. UMBGROVE and ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1898, **17**, 270—286).—*Dipropyldinitroxamide*, $C_2O_2(NPr \cdot NO_2)_2$, prepared by leaving dipropyloxamide in contact with six times its weight of concentrated nitric acid for 48 hours, and pouring the product into ice cold water, crystallises from alcohol in large tables, and melts at 44°. When dissolved (65 grams) in concentrated aqueous ammonia (150 c.c.), oxamide separates, whilst the ammonium derivative of propylnitramine remains dissolved; on adding dilute sulphuric acid to the clear solution, nearly the theoretical quantity of propylnitramine is obtained.

Ethylpropylnitramine, prepared by boiling a mixture of the potassium derivative of ethylnitramine (26 grams), propylic iodide (32 grams), and methylic alcohol (100 c.c.) during 30 hours, is a colourless liquid with a characteristic odour; it boils at 108° under a pressure of 22 mm., and has a sp. gr. = 1·028 at 15°. It dissolves in concentrated sulphuric acid without evolution of gas, giving rise, apparently, to nitrosulphuric acid and a substance possessing cupric-reducing power, which is probably a hydroxylamine or an imine. From the lower fractions obtained in purifying the crude ethylpropylnitramine by fractional distillation, a *substance* isomeric with the latter was isolated, differing from it in boiling point (65° under a pressure of 20 mm.) and in its behaviour with concentrated sulphuric acid. On heating ethylpropylnitramine with 10 per cent. aqueous potash for 9 hours at 150—160°, it is decomposed into propylamine, nitrous acid, and acetaldehyde; this is in accordance with van Erp's views (Abstr., 1895, i, 590; and 1897, i, 6) regarding the action of alkalis on mixed aliphatic nitramines. It appears that, in this decomposition, the heavier radicle separates combined with the amido-group, and the lighter in the form of an aldehyde.

The principal product formed on leaving the silver derivative of propylnitramine (82 grams) in contact with ethylic iodide (60 grams) dissolved in ether (500 grams) during 12 hours in the dark, and subsequently heating the mixture during 6 hours at 50°, is *iso-ethylpropylnitramine*; this distils unchanged at 58·5° under a pressure of 16 mm., has a sp. gr. = 0·9755 at 15°, and does not give a coloration with an acetic acid solution of α-naphthylamine, either alone or in presence of zinc. It differs in this respect from an isomeric *substance* formed simultaneously, which decomposes when distilled into nitrogen, water, acetaldehyde and propaldehyde; together with this unstable isomeride, a small quantity of ethylpropylnitramine is also formed. On heating iso-ethylpropylnitramine with 10 per cent. aqueous potash,

nitrogen is evolved, and propaldehyde appears to be formed, although this immediately polymerises, giving a resin. ·

Isopropylethylnitramine, prepared by acting on the silver derivative of ethylnitramine with an ethereal solution of propylic iodide, boils at 65° under a pressure of 20 mm., and has a sp. gr. = 0·9783 at 15°; at the same time, propylethylnitramine is formed, together with an isomeric *substance*, which decomposes when heated, giving nitrogen and propaldehyde.

When isopropylethylnitramine is heated with 10 per cent. aqueous potash, it gives rise to nitrogen and acetaldehyde, in accordance with van Erp's rule (*loc. cit.*).

Isopropylmethylnitramine, prepared by leaving the silver derivative of methylnitramine in contact with propylic iodide dissolved in ether during 5 days at the ordinary temperature, boils at 51° under a pressure of 18 mm., and has a sp. gr. = 1·012 at 15°; although no gas is evolved when it is heated at 100°, it gives a marked coloration with an acetic acid solution of α-naphthylamine. When decomposed by aqueous potash, it apparently gives rise to formaldehyde.

<div align="right">W. A. D.</div>

Action of Sulphuric Acid on Aliphatic Nitramines and their Isomerides. By ANTOINE P. N. FRANCHIMONT and HERM. UMBGROVE (*Rec. Trav. Chim.*, 1898, **17**, 287—295).—Concentrated sulphuric acid acts in the same manner on the silver and mercury derivatives of methylnitramine as on methylnitramine itself; in each case, nearly the theoretical quantity of nitrous oxide is evolved, no other gas being formed. From ethylnitramine, however, and its potassium derivative, a small quantity of an inflammable gas, probably an olefine, was also obtained, and the same is true of propyl- and butyl-nitramine.

The behaviour of ethylpropylnitramine with concentrated sulphuric acid has been dealt with in the preceding abstract; the action is the same, but slower, when 40 per cent. sulphuric acid is employed, partial decomposition only taking place. The isodialkylnitramines are, however, rapidly decomposed by this acid at the ordinary temperature, giving nitrous oxide and two alcohols, that formed by the alkyl radicle directly attached to the nitrogen also giving rise, as a rule, to an olefine, except in the case when the radicle is methyl. This behaviour was verified in the case of iso-ethylmethyl-, isomethylethyl-, isodiethyl-, iso-ethylpropyl-, isopropylethyl-, and isopropylmethyl-nitramines. The ease with which the isodialkylnitramines undergo decomposition when treated with 40 per cent. sulphuric acid is explained by attributing to them the general formula $NR:NO·OR$; or, assuming that the acid nitramines have the general formula $O{<}^{NHR}_{N}{>}O$ (Brühl), by giving the neutral isonitramines the general structure $O{<}^{NR}_{N·OR}$.
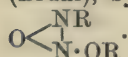
<div align="right">W. A. D.</div>

Neurine and its Derivatives. By WL. GULEWITSCH (*Zeit. physiol. Chem.*, 1898, **26**, 175—188).—The author describes the appearance, as seen with the unassisted eye and with the microscope, of

precipitates obtained with dilute solutions of synthetically prepared neurine hydrochloride and the usual reagents for alkaloids. These precipitates obtained with dilute solutions of neurine are far less soluble than those from choline. Contrary to Brieger's observation, the author finds that phosphotungstic acid gives a precipitate with neurine hydrochloride which is distinctly visible even in solutions containing only $\frac{1}{2000}$th of the base.

Neurine picrate forms golden-yellow needles melting at 263—264°; it is very insoluble in cold water and alcohol. Neurine platino-chloride melts at 195·5—198°, contains no combined water, and differs in its crystalline form from the corresponding choline salt. The aurichloride, $C_5H_{12}NAuCl_4$, forms golden-yellow needles melting at 228—232°, and contains no water of crystallisation. On the addition of mercurous chloride to an alcoholic solution of neurine hydrochloride, two double *salts* are precipitated; the less soluble, $C_5H_{12}NCl,6HgCl_2$, forms colourless, tabular crystals and melts at 230·5—234°; the more soluble, $C_5H_{12}NCl,HgCl_2$ crystallises in aggregates of narrow prisms and melts at 198·5—199·5°. Dilute solutions of neurine are not decomposed on boiling, but concentrated solutions give off trimethyl-amine. Neurine hydrochloride, when recrystallised from water, has no tendency to take up one molecule of the solvent and become trans-formed into choline hydrochloride. G. T. M.

Constitution of Ornithine and Arginine. By Ernst Schulze and Ernst Winterstein (*Zeit. physiol. Chem.*, 1898, **26**, 1—14. Compare Abstr., 1898, i, 281).—Ornithine, $C_5H_{12}N_2O_2$, was originally discovered by Jaffé (Abstr., 1878, 585), who suggested that its consti-tution might be that of a diamidovaleric acid; it does, in fact, closely resemble the diamidopropionic acid prepared synthetically by E. Klebs (Abstr., 1894, i, 439). Arginine, $C_6H_{14}N_4O_2$, prepared either from the seedlings of *Lupinus luteus* or by heating albumin with hydrochloric acid, yields ornithine and carbamide when hydrolysed with baryta water. Ornithuric acid, the dibenzoyl derivative of the former base (Jaffé, *loc. cit.*), is obtained from the crude product of reaction by the Schotten-Baumann method; this compound is hydrolysed by con-centrated hydrochloric acid, first into a monobenzoyl derivative, and then into ornithine, the yield of benzoic acid and ornithine dihydro-chloride being almost theoretical. Ornithine, on treatment with nitrous acid, loses the whole of its nitrogen, but the hydroxy-acid which should be formed has not been investigated. Phenanthraquinone gives no quinoxaline derivative with ornithine, and the authors there-fore suppose that the amidogen groups are not attached to contiguous carbon atoms. If ornithine be assumed to be a diamidovaleric acid, then arginine might have the following constitution,

$$NH{:}C(NH_2){\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH,$$
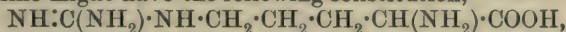
which resembles those of glycocyamine and creatine.

The yield of ornithine from arginine is only 40 per cent. of the theoretical quantity. This may be due, as in the case of creatine, to the fission of the molecule taking place in two ways, but no other well-characterised product of hydrolysis has yet been isolated.

G. T. M.

The So-called Nitroazoparaffins. By EUGEN BAMBERGER (*Ber.*, 1898, **31**, 2626—2635).—In accordance with modern views, the "nitroazoparaffins" of Victor Meyer must be regarded as hydrazones containing the grouping $\cdot C(NO_2):N\cdot NH\cdot$, and, therefore, as true nitro-compounds, whilst their salts must be looked on as derived from the tautomeric isonitro-azo-compounds, the above group having become $\cdot C(NOOH)\cdot N:N\cdot$.

When "nitroazoparaffins" are subjected to alkaline hydrolysis, they are decomposed with production of acidylhydrazines and nitrous acid. Thus "phenyl-nitroazopropane," or nitropropionalde(phenyl)-hydrazone,* as the author prefers to term it, when heated on the water-bath, with a 1 per cent. solution of soda, is almost quantitatively converted into β-propionylphenylhydrazine, probably in accordance with the equation, $NO_2\cdot CEt:N\cdot NHPh + H_2O = COEt\cdot NH\cdot NHPh + HNO_2$.

Nitroacetalde(phenyl)hydrazone, $NO_2\cdot CMe:N\cdot NHPh$, is produced in nearly theoretical amount by the foregoing process. Nitroethane (10 grams) is quickly dissolved in an ice cold solution of soda (5·2 grams) in water (3 grams) and mixed at once with an ice cold solution of the diazonium acetate made by dissolving aniline (12 grams), concentrated hydrochloric acid (30 grams), sodium nitrite (9·4 grams), and crystallised sodium acetate (44·4 grams) in water (2 litres). The substance separates quickly as a yellow oil, which soon solidifies; it does not exhibit either Meyer's or Konowaloff's reaction, and cannot, therefore, be the "iso-" form, $NOOH:CMe\cdot N:NPh$. It crystallises from alcohol in golden-yellow, and from benzene in orange-red, leaflets, and melts at 141—142°. It decomposes slightly when kept in a closed vessel, and then has an odour of acetic acid; in one instance, it decomposed, giving nitrous and acetic acids and diazobenzene nitrate.

When nitroacetalde(phenyl)hydrazone is warmed with a dilute solution of soda in dilute methylic alcohol for 2 hours, it is decomposed, giving an appreciable quantity of an isodiazotate, ammonia, phenyl-hydrazine, and a neutral oil, but the principal product is β-acetyl-phenylhydrazine.

Nitropropionalde(phenyl)hydrazone, $NO_2\cdot CEt:N\cdot NHPh$, prepared by a method similar to that used in the case of the acetaldehyde compound, forms hard, orange-yellow crystals, and melts at 98·5—99·5° (compare Meyer, this Journal, 1876, ii, 93). It does not, as stated by Meyer, give an immediate violet-red coloration when treated with strong sulphuric acid, but a fiery-red, the violet tone being a later development; a similar statement holds true in the case of the acetaldehyde compound. Nitropropionalde(phenyl)hydrazone, is, as has already been mentioned, almost completely converted into nitrous acid and β-propionylphenylhydrazine when warmed with dilute soda.

Nitrovaleralde(phenyl)hydrazone, $C_4H_9\cdot C(NO_2):N\cdot NHPh$, is obtained when nitropentane is treated with the diazonium acetate; it exists in two forms. The β-*modification* obtained by crystallising the substance from alcohol, separates in golden-yellow leaflets having a bronze-like lustre, and melts at 92·5—93°, dissolves readily in acetone, and decomposes when kept for a long time in a closed vessel; its solution in sulphuric acid is at first fiery red, but gradually becomes violet-red

* The author omits the "phenyl" in his paper.—[EDITORS.]

spontaneously, and at once on the addition of dichromate. The *α-modification* obtained from the former by boiling it with heavy petroleum, separates from the solution on cooling in long, silky needles, which are orange-red by reflected and golden-yellow by transmitted light, and have a metallic-blue reflex; it has the same composition as the α-form, but melts at 51·5—52°, and is very readily dissolved by light petroleum; it may be converted into the β-modification by dissolving it in boiling alcohol, and if the melted substance is allowed to solidify, it melts once more at 86—87°, indicating a more or less complete conversion into the β-form; a similar change is found to have occurred when its solution in alkalis is precipitated by means of an acid. By treatment with alkali, β-nitrovaleralde(phenyl)hydrazone is converted into β-valerophenylhydrazide; the latter melts at 112—112·5° and not at 101° as stated by Autenrieth (Abstr., 1888, 251).   A. L.

Formhydroxamic Acid.—By JOHN U. NEF (*Ber.*, 1898, **31**, 2720—2721).—In view of the paper recently published by Schroeter (Abstr., 1898, i, 623), the author points out that investigations on formhydroxamic acid and its derivatives are in progress in his laboratory. The ethers of this acid can be obtained by heating formic acid with α-alkylhydroxylamines. Benzylhydroxamic acid, for example, can readily be prepared in this way, and is a thick oil with strongly acid properties.   A. H.

Action of Semicarbazide on Formaldehyde. By JOHANNES THIELE and JAMES BAILEY (*Annalen*, 1898, **303**, 91—93).—When a 4 per cent. solution of formaldehyde is added to aqueous semicarbazide hydrochloride, a gelatinous precipitate is formed, and this *compound*, after being washed with water and dried at 95°, has the composition $C_5H_{10}N_6O_2 + \frac{1}{2}H_2O$; it is, therefore, a hydrated condensation product of semicarbazide (2 mols.) with formaldehyde (3 mols.). H. Thoms (*Ber. deutsch. Pharm. Ges.*, **7**, 5) has recently obtained a normal product of condensation. The substance dissolves in 60 per cent. hydrocyanic acid, yielding a compound which crystallises from dilute acetic acid, and melts at 127·5°; no definite formula has been assigned to it.   M. O. F.

Aldehyde-ammonia. By ROBERT DE FORCRAND (*Compt. rend.*, 1898, **126**, 248—250).—The author's calorimetric experiments confirm those by which Delépine (Abstr., 1898, i, 462) demonstrates that aldehyde-ammonia in the solid state consists of the more or less polymerised hydrate of ethylidenimine, and that, when dissolved in water, a gradual change into the simple form takes place.

Two series of calorimetric determinations were made on the heat developed by the action of dilute sulphuric acid on solutions of aldehyde-ammonia which had been kept for different periods of time.

In one case, the aldehyde-ammonia solution was prepared by adding weak ammonia to a dilute solution of aldehyde, and in this series of determinations the heat effect at first decreased until a minimum was reached after 8 days, and then increased until the end of 50 days.

When the solution was prepared by dissolving solid aldehyde-ammonia in water, the heat developed by the action of the acid was

least after 7 minutes, and gradually increased until the end of 50 days. In the first series, there is a rapid change of aldehyde-ammonia into polymerised ethylidenimine, and, at the same time, this polymeride slowly passes into the simple form; in the second series, the polymeride gradually dissociates into the simple imine.   G. T. M.

Amidoaldehydes. By EMIL MAASS and RICHARD WOLFFENSTEIN (*Ber.*, 1898, **31**, 2687—2692. Compare Abstr., 1898, i, 44).—For reasons which are discussed in the original paper, the authors regard those amidoaldehydes which are convertible into piperidine derivatives as capable of acting in accordance with the tautomeric formula, $:C_5H_8\cdot NH:O$; from this point of view, they belong to the group of oxides obtained by the action of hydrogen peroxide on 1-alkylpiperidine bases (Wernick and Wolffenstein, Abstr., 1898, i, 536). The facts which have led to this conclusion are as follows.

The benzoyl derivative of orthamidomethylphenylacetaldehyde (Abstr., 1898, i, 44) yields benzoic acid on oxidation with potassium permanganate. Benzoic acid is also produced by the oxidation of the *benzoyl* derivative of δ-amidovaleraldehyde (Abstr., 1892, 1484), which melts at 66°; the other product is a hygroscopic syrup which is also formed when piperidine is oxidised with potassium permanganate. Carbon bisulphide converts δ-amidovaleraldehyde into the dithiocarbamate of piperidine (m. p. 169—171°), and by its action on amidovaleropropaldehyde, gives rise to the *dithiocarbamate* of coniine, which melts at 58—61°.

In the behaviour of amidovaleraldehyde towards nitrous acid, however, it resembles ordinary amidoaldehydes.   M. O. F.

Action of Water on Acraldehyde Dibromide. By CORNELIS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1898, **17**, 259—262).—Although acraldehyde dibromide is converted into bromacraldehyde when boiled with a 50 per cent. aqueous solution of sodium acetate (Piloty and Stock, Abstr., 1898, i, 402), it apparently gives rise to *glyceraldehyde* when left in contact with water, either at the ordinary temperature, or, better, at that of the water-bath. On removing the hydrobromic acid from the solution by successive treatment with lead carbonate, hydrogen sulphide, and moist silver oxide, and subsequently concentrating in a vacuum, a syrup is obtained which reduces Fehling's solution, and gives rise to glycerosazone when mixed with a solution of phenylhydrazine acetate.   W. A. D.

[NOTE BY ABSTRACTOR.—Since the original paper was published, Wohl (*Ber.*, 1898, **31**, 2394) has prepared glyceraldehyde from the acetal of acraldehyde, in the form of a white, crystalline powder.]

Acetylmethylheptenone (2·Methyl-2-nonene-6 : 8-dione). By PHILIPPE BARBIER and GEORGES LESER (*Bull. Soc. Chim.*, 1897, [iii], **17**, 748—751).—Natural methylheptenone (2-methyl-2-heptene-6-one) readily reacts with ethylic acetate in the presence of sodium, with the formation of *acetylmethylheptenone*, $CMe_2:CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot COMe$. The latter is purified by conversion into its copper derivative, a pale

blue, crystalline powder melting at 132—133°, from which it is regenerated by the action of dilute sulphuric acid. Acetylmethylheptenone is a colourless liquid of powerful aromatic odour and having a sp. gr. $= 0.954$ at 0°. It boils at 114—115° under a pressure of 15 mm., and at 233—234°, with slight decomposition, at the ordinary pressure. Treatment with the theoretical quantities of hydroxylamine hydrochloride and sodium carbonate converts it into the *oxazole*, $CMe_2:CH\cdot CH_2\cdot CH_2\cdot C{<}^{CH:CMe}_{N-O}$, which boils at 118—119° under a pressure of 14 mm., whilst the *dioxime*, a crystalline substance melting at 109—110°, is also formed.

Acetylmethylheptenone forms a sodium derivative,

$$CMe_2:CH\cdot CH_2\cdot CH_2\cdot CO\cdot CHNa\cdot COMe,$$
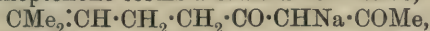
which, when warmed for some hours with ethylic monochloracetate, is converted into a mixture of the ethylic salts of 2-methyl-2-hexenoic acid, levulinic acid, and 2-methyl-2-nonene-6-onoic acid. The first two of these compounds are formed by the action of alcohol, and the third by the action of water, on the normal product of the reaction, which would have the composition

$$CMe_2:CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH(COMe)\cdot CH_2\cdot COOEt.$$
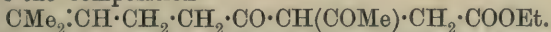
Ethylic 2-methyl-2-hexenoate, $CMe_2:CH\cdot CH_2\cdot CH_2\cdot COOEt$, is a colourless liquid of agreeable odour which boils at 182—184° and has a sp. gr. $= 0.928$ at 0°. On hydrolysis, it yields *2-methyl-2-hexenoic acid*, which is a colourless liquid boiling at 216—218°.

Ethylic 2-methyl-2-nonene-6-onoate boils at 152—154° under a pressure of 14 mm. and has a sp. gr. $= 0.988$ at 0°. The corresponding *acid* crystallises from light petroleum in colourless needles melting at 57°. The ethylic salt forms a *phenylhydrazone*, which melts at 93° and boils at 235—240° under a pressure of 15 mm.

The sodium derivative of acetylmethylheptenone reacts with ethylic iodide to form *acetylmethylethylheptenone*, which boils at 133—135° under a pressure of 15 mm. N. L.

Conversion of Ketones into Diketones. III. By MICHELE FILETI and GIACOMO PONZIO (*J. pr. Chem.*, 1898, [ii], **58**, 362—367).—Further investigations have confirmed the conclusions already arrived at (Abstr., 1897, i, 317).

Ethyl butyl ketone yields a mixture of two diketones, *acetylvaleryl* and *propionylbutyryl*, and two dinitrohydrocarbons; of the former, the mixture of *dioximes* was so far separated by fractional crystallisation from dilute alcohol that fractions melting at 168—170° and 141—144° were obtained; as regards the dinitrohydrocarbons, potassiodinitroethane is more soluble than the corresponding butane derivative. Ethyl amyl ketone behaves in a similar manner; acetylhexoyl and propionylvaleryl are the diketones; the *dioxime* and *osazone* of the latter melt at 139—141° and 96—97° respectively; as regards the dinitrohydrocarbons, potassiodinitroethane is more soluble than the corresponding pentane derivative. Ethyl isoamyl ketone yields acetylisohexoyl and dinitroethane only; the dioxime of the former was also prepared from ethylic isoamylacetoacetate. Ethyl isohexyl ketone yields acetylisoamylacetyl and dinitroethane only. C. F. B.

Acetylation with the help of Sulphuric Acid. By ZDENKO H. SKRAUP (*Monatsh.*, 1898, **19**, 458—460).—The author points out that Franchimont (Abstr., 1880, 159) was the first to draw attention to the value of sulphuric acid as an addition to acetic anhydride in acetylating (compare Thiele, Abstr., 1898, 469), and the method has long been employed in the author's laboratory. The reaction is liable to become uncontrollable unless precautionary measures are taken.

By the action of acetic anhydride containing less than 1/100 per cent. of its weight of sulphuric acid on mucic acid, tetracetylmucic acid is easily produced in amount equal to 79 per cent. of that theoretically possible. By the usual method of heating the acid with acetic anhydride and anhydrous sodium acetate, only amorphous products are obtained. With smaller quantities of sulphuric acid (1/10000 per cent.), the reaction still goes on, but is probably incomplete.

The method of estimating acetyl used by Wenzel (Abstr., 1898, i, 234) was published first by Franchimont (*Ber.*, 1879, **12**, 1940), and modified later by the author (Abstr., 1894, i, 15).   A. L.

Preparation of Zinc Valerate. By DIOSCORIDE VITALI (*L'Orosi*, 1898, **21**, 114—117).—One hundred parts of dry sodium valerate and 117 parts of crystallised zinc sulphate are separately dissolved in the smallest possible quantity of hot water, the solutions mixed, the liquid evaporated to dryness at a temperature not exceeding 70°, and the finely powdered residue extracted with 95 per cent. alcohol. On concentrating the alcoholic extract by evaporation at 70°, zinc valerate is obtained in a very pure crystalline condition. This process is simpler and more economical than those commonly employed.
          N. L.

Wax of the Humble Bee. By ERNST E. SUNDVIK (*Zeit. physiol. Chem.*, 1898, **26**, 56—59).—Samples of wax taken from the nests of *Bombus muscarum* and *B. lapidarius* have the same chemical properties. The mixture of wax and pollen, freed from eggs and larvæ, and extracted with ether or chloroform, yields a crude wax of brownish-yellow colour, melting at 35—40°, and having an agreeable odour resembling honey. This substance still contains fat and colouring matter. The principal constituent of the wax is an alcoholic substance, which is freed from glycerides by treating the partly purified product with weak potash on the water-bath. After repeated crystallisations from alcohol, the unaltered residue melts at 74—75°, and its composition agrees with the formula $C_{34}H_{70}O$; it forms flexible, woolly needles which can be easily kneaded into a pale yellow cake. A *benzoyl* derivative, $C_{34}H_{69}OBz$, obtained by heating the substance with benzoic anhydride at 150—160°, crystallises from alcohol, benzene, and petroleum, and melts at 55°.   G. T. M.

Ethylic β-Isopropylacetobutyrate and Stereoisomeric Di-isopropylbutenedicarboxylic Acids. By PHILIPPE BARBIER and V. GRIGNARD (*Compt. rend.*, 1898, **126**, 251—253).—Ethylic isobutylideneacetoacetate and ethylic malonate suffer condensation in the presence of potassium ethoxide, yielding a liquid which, when

distilled, first under ordinary and subsequently under reduced pressure, gives rise to two substances; the chief product, a colourless liquid boiling at 170° under atmospheric pressure, consists of *ethylic β-isopropylacetobutyrate*, $CH_2Ac \cdot CHPr^\beta \cdot CH_2 \cdot COOEt$; the product obtained in less quantity is an unstable intermediate *compound*, $COOEt \cdot CHAc \cdot CHPr^\beta \cdot CH(COOEt)_2$, boiling at 189—191° under a pressure of 10 mm., which passes into the preceding substance by the loss of two COOEt groups.

When ethylic β-isopropylacetobutyrate is treated with sodium ethoxide, two molecules of the former coalesce, and condensation takes place, accompanied by the elimination of two molecules of acetone. The *ethereal* salt, $C_{16}H_{28}O_4$, which is obtained, boils at 156° under a pressure of 10 mm., and on hydrolysis furnishes a mixture of two isomeric *di-isopropylbutenedicarboxylic acids*, having the formula $COOH \cdot CH_2 \cdot CPr^\beta : CPr^\beta \cdot CH_2 \cdot COOH$; one crystallises in needles melting at 156—158°, and the other in colourless plates melting at 117—119°. The stereoisomeric relationship of these isomerides has not yet been determined.   G. T. M.

Syntheses with Ethylic Cyanacetate. By TIMOTHÉE KLOBB (*Ann. Chim. Phys.*, 1897, [vii], 10, 145—214).—*Ethylic isovaleryl-cyanacetate*, $CHMe_2 \cdot CH_2 \cdot CO \cdot CH(CN) \cdot COOEt$, produced by adding an ethereal solution of isovaleric chloride to an alcoholic solution of ethylic cyanacetate in the presence of sodium ethoxide, separates in white needles when the oily product is cooled to −36°; it melts at +21°, boils at 138—140° under a pressure of 21 mm., at 144—148° under 31 mm., and decomposes when distilled at the ordinary pressure; its specific gravity = 1·030 at 24°. The substance is a strong acid, not only decomposing carbonates, but its alcoholic solution dissolves the metals, magnesium, zinc, iron, aluminium, copper, cobalt, and nickel, with the evolution of hydrogen; silver, bismuth, and antimony are not attacked. The *magnesium, ferrous*, and *copper* derivatives obtained in this manner by the displacement of the hydrogen in the CH group are described.

Methylic isovalerylcyanacetate, prepared like the ethylic salt, crystallises in rhombic plates melting at 41—42°, and boils without decomposition at 171—172° under a pressure of 100 mm.; its *sodium, calcium, barium*, and *silver* derivatives are crystalline. Both ethereal salts are insoluble in water, but dissolve easily in the usual organic solvents.

When boiled with aqueous potash, they undergo hydrolysis, ammonia, the potassium salts of carbonic, acetic, and isovaleric acids and the corresponding alcohol being produced; long continued boiling with water results in the formation of tarry products and a small quantity of a *compound* having the formula $C_{14}H_{22}N_2O$, and crystallising in white needles melting at 133—134°.

The preparation of the alkylic derivatives of diphenacylcyanacetic acid (ββ-dibenzoylcyanisobutyric acid) is given in detail; the *propylic* salt, obtained by the action of bromacetophenone on methylic cyanacetate, dissolved in propylic alcohol, in the presence of sodium propyloxide, crystallises from alcohol in nacreous leaflets and melts at 114°. The isobutylic salt could not be obtained by this method; the

methylic and ethylic salts have been previously described (see Abstr., 1894, i, 592; 1897, i, 531). Phenylhydrazine gives rise to no definite hydrazones with these ethereal salts. On hydrolysis with boiling alkalis, they yield diphenacylacetic acid ($\beta\beta$-dibenzoylisobutyric acid).

The preparation of the alkylic phenacylcyanacetates (a-cyano-β-benzoylpropionates) is described at some length; an account of these compounds and of the free acid has already been published (see Abstr., 1896, i, 126). β-Benzoylpropionic acid is the final product of the action of potash on these ethereal salts.

The syntheses based on the displacement of the hydrogen of the group CH in the above ethereal salts have already been studied (Abstr., 1896, loc. cit., and 1897, i, 419; 1898, i, 586); the preparation of the methylic, ethylic, and benzylic substitution products are fully described in the paper. Ethylic and methylic a-cyano-β-acetylpropionates have already been described (Abstr., 1896, loc. cit.).

<div align="right">G. T. M.</div>

Constitution of Tetric Acid and of the Lactone of γ-Hydroxydimethylacetoacetic Acid. By MAX CONRAD and RICHARD GAST (Ber., 1898, **13**, 2726—2731).—Methylic monobromodimethylacetacetate, which has been previously described (Abstr., 1897, i, 321), boils at 225—230° under atmospheric pressure, undergoing slight decomposition. When the acetate prepared from this compound by means of potassium acetate is kept for some months at the ordinary temperature, it yields methylic acetate and the lactone of γ-hydroxydimethylacetoacetic acid (2 : 2-dimethyl-3-butanone-4-oloic acid, $CMe_2{<}^{CO \cdot CH_2}_{CO \cdot O}$, which is a colourless oil of sp. gr. = 1·147 at 18°/15°, and boils at 208—212° without decomposing. The dilute alcoholic solution gives no reaction with ferric chloride. Bromine converts the lactone into a *monobromo*-derivative, which is decomposed by water with formation of the lactone of dihydroxydimethylacetoacetic acid. Aniline converts the original lactone into a *derivative*, $C_{12}H_{13}O_2N$, which crystallises in compact, lozenge-shaped crystals melting at 88° and boiling at 300—310°; this compound, which is decomposed by aqueous baryta and by platinic chloride, probably has the constitution $CMe_2{<}^{CO—O}_{C(NPh)}{>}CH_2$. The lactone readily reacts with hydroxylamine hydrochloride to form an *oximidolactone*, $OH \cdot N{:}C{<}^{CH_2—O}_{CMe_2 \cdot CO}$, which melts at 134°, and gives no coloration with ferric chloride; the corresponding *phenylhydrazone* melts at 131°, and is sparingly soluble in light petroleum. *Methylic tetrate*, $OMe \cdot C{<}^{CH_2—O}_{CMe \cdot CO}$, prepared by the action of methylic iodide on silver tetrate, is a colourless liquid boiling at 215—220°; it is isomeric with the lactone just described, but does not yield derivatives with hydroxylamine or phenylhydrazine, whilst acids reconvert it into tetric acid.

The fact that the lactone of γ-hydroxydimethylacetoacetic acid is so

dissimilar from tetric acid both in chemical behaviour and boiling point renders it improbable that the latter is the lactone of γ-hydroxy-methylacetoacetic acid, having the formula

$$CHMe\begin{cases} CO\cdot O \\ CO\cdot CH_2 \end{cases}$$
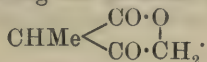
A. H.

Reduction of Aconic Acid to Paraconic Acid. By HANS REITTER (*Ber.*, 1898, **31**, 2722—2725).—Aconic acid is readily converted into paraconic acid when it is treated with glacial acetic acid and zinc dust, although Fittig (*Annalen*, 1883, **216**, 97) was unable to effect this reduction by means of sodium amalgam. The ready formation of paraconic acid affords further evidence in favour of the formula $COOH\cdot C\begin{cases} CH-O \\ CH_2\cdot CO \end{cases}$ for aconic acid proposed by Fittig.

A. H.

Synthesis of Terebic Acid. By EDMOND E. BLAISE (*Compt. rend.*, 1898, **126**, 349—351).—Ethylic bromosuccinate and acetone are mixed together in the presence of a copper–zinc couple and the mixture is occasionally shaken during 24 hours. The double zinc compound produced is decomposed by dilute sulphuric acid, and the ethylic terebate is extracted by means of ether and hydrolysed by aqueous potash. The acid is liberated by hydrochloric acid and purified, first by conversion into its soluble barium salt, and subsequently by recrystallisation from water and alcohol; it melts at 174°, and is further identified by conversion into methyl-2-pentanolide. The yield of terebic acid from ethylic bromosuccinate is 10—12 per cent., that from pinene is less than 2.

G. T. M.

Tautomeric Forms of Ethylic Isaconitate and of Ethylic Dicarboxyglutaconate. By MAX GUTHZEIT (*Ber.*, 1898, **31**, 2753—2758).—Ethylic isaconitate is a thin, colourless liquid which boils at 178—180° under a pressure of 20 mm. and has the sp. gr. = 1·1291 at 20°/20°.

This constitutes the enolic form of the compound, and gives a deep blue coloration with ferric chloride, whilst it also forms a copper salt, and is at once coloured deep yellow by sodium carbonate. This form is always obtained by the ordinary methods of preparation, but changes very slowly, if kept, into the ketonic or true form, which is also produced in a few hours when a small amount of piperidine is added to the enolic form.

The ketonic form is a very viscid, deep yellow oil which cannot be distilled without undergoing decomposition, and has a sp. gr. = 1·1432 at 20°/20°. It gives no coloration with ferric chloride, does not yield a copper salt, and is only slowly coloured yellow by sodium carbonate. When it is dissolved in alcoholic sodium ethoxide and the solution acidified, the enolic form is regained. Both forms have the same molecular weight as determined by the boiling point method.

The two forms of this compound probably have the following constitutions,

$COOEt\cdot CH:CH\cdot CH(COOEt)_2$; $COOEt\cdot CH:CH\cdot C(COOEt):C(OH)\cdot OEt$

Ethylic dicarboxyglutaconate appears also to exist in two forms, the enolic form being that which has previously been described, whilst the

ketonic or true form, which is produced by the action of piperidine and is also formed when the enolic form is kept for a long time, crystallises in monosymmetric crystals melting at 101—102°. The latter have only been obtained in very small amount, and are being further investigated.   A. H.

Condensation of Ethylic Malonate with Aldehydes under the Influence of Ammonia and Organic Amines. By EMIL KNOEVENAGEL (*Ber.*, 1898, **31**, 2585—2595. Compare Abstr., 1894, i, 570, &c.)—Methylenebispiperidine and methylenebisaniline react readily with ethylic malonate when heated with it on the water-bath, yielding ethylic methylenebismalonate. When aniline is added to ethylic malonate mixed with formaldehyde, no action takes place at the ordinary temperature, and methyleneaniline does not react with ethylic malonate to form ethylic methylenebismalonate. The best method for the production of the latter substance is to add a small quantity of an amine, usually piperidine or diethylamine, to a mixture of formaldehyde and ethylic malonate mixed in the requisite proportions.

Ethylic ethylidenebismalonate, prepared in a manner similar to the above, boils at 208—209° under a pressure of 17 mm.; it is accompanied by ethylic ethylidenemalonate. The derived β-methylglutaric acid melts at 87°, and its anhydride at 47°. *Ethylic isobutylidenebismalonate* boils at 198° under a pressure of 12 mm., and β-isopropylglutaric acid prepared from it melts at 96·5—97° (Schryver, Trans., 1893, 1345, gives 99—100°), and affords a *silver* salt, $C_8H_{12}O_4Ag_2$, which is sparingly soluble in water. *Ethylic β-isopropylglutarate* is a thick oil having a pleasant odour, and boils at 250° under atmospheric pressure.

Ethylic isoamylidenebismalonate, $C_{19}H_{32}O_8$, boils at 204° under a pressure of 15 mm. *β-isobutylglutaric acid* crystallises in long, white needles, and melts at 48°; it is very soluble in ether, alcohol, glacial acetic acid, and water, and somewhat readily in carbon bisulphide and light petroleum; its *copper*, *zinc*, and *lead* salts are insoluble in water, and the *silver* salt, $C_9H_{14}O_4Ag_2$, is a white, curdy precipitate. *Ethylic œnanthylidenebismalonate*, $C_{21}H_{36}O_8$, boils at 195° under a pressure of 16 mm.; the corresponding *β-hexylglutaric acid* was obtained in very small amount, and melted at 215—236°.

Aromatic aldehydes and ethylic malonate condense in molecular proportion under the influence of amines. Ethylic benzylidene malonate is easily obtained by treating a mixture of benzaldehyde (1 mol.) and dry ethylic malonate (1 mol.), with a little piperidine or alcoholic ammonia. [With F. GIESE.]—*Ethylic cumylidenemalonate*, $C_{17}H_{22}O_4$, is a light yellow oil, and boils at 205—208° under 15 mm. pressure.

[With H. HOFFMANN.]—*Ethylic paranitrobenzylidenemalonate*, $C_{14}H_{14}O_6N$, forms colourless needles and melts at 94°; it dissolves readily in hot alcohol, light petroleum, and benzene, but only sparingly in ether.

Ethylic coumarincarboxylate, $\begin{array}{c} C(COOEt){:}CH \\ | \qquad\qquad\quad {>}C_6H_4 \\ CO{-}\!\!-\!\!-\!\!-\!\!-\!\!-O \end{array}$, is made by the condensation of salicylic aldehyde with ethylic malonate by means

of piperidine or ammonia; it forms crystals, and melts at 94°; coumarincarboxylic acid melts at 185—187°.

[With A. GROOS.]—*Ethylic anisylidinemalonate*, $C_{15}H_{18}O_5$, boils at 200—217° under 14 mm. pressure, and melts at 38—40°; it dissolves readily in ether, benzene, and alcohol. *Ethylic methylsalicylidene-malonate*, $C_{15}H_{18}O_5$, boils at 193—195° under a pressure of 14 mm., and could not be soldified.

[With F. GIESE.]—Ethylic piperonylidenemalonate boils at 216—219° under a pressure of 11 mm., crystallises from alcohol in beautiful, colourless prisms, and melts at 63°; it is readily soluble in cold benzene and acetic acid, and in warm ether and alcohol, and is sparingly soluble in light petroleum.

Ethylic furfurylidenemalonate, which may be produced in several different ways by the condensation of furfuraldehyde and ethylic malonate, is obtained in small amount by merely warming the components together on the water-bath, but the yield is greatly augmented by the addition of a little piperidine.   A. L.

Uric Acid and the Murexide Reaction. By DIOSCORIDE VITALI (*L'Orosi*, 1898, 21, 73—80).—The fact that the presence of small quantities of iodides in urine cannot be directly demonstrated by the usual methods has been attributed to the oxidation of organic compounds, especially uric acid, by the iodine at the moment of its liberation, with simultaneous formation of hydriodic acid. The production of the latter is shown by the immediate liberation of iodine on adding iodic acid, and by means of this reagent traces of iodine in the form of iodides may readily be detected in urine. If, moreover, a solution of iodine be gradually added to a solution of potassium urate mixed with a little starch paste, no blue coloration appears until a considerable amount of iodine has been absorbed; the liquid at the same time becomes acid from the production of hydriodic acid, and deposits a crystalline precipitate of uric acid. A portion of the latter is simultaneously oxidised to carbamide and alloxan, as was proved by the isolation of urea oxalate and by the fact that the liquid gave the murexide reaction when evaporated to dryness and gently heated. This formation of murexide (ammonium purpurate) is probably due to the action of the ammonia, produced by the decomposition of the carbamide, on the alloxantin formed by the reduction of the alloxan by hydriodic acid. Instead of iodine, chlorine, bromine, iodic acid, and nitric acid may be used. In the last case, the necessary reduction in the latter phase of the reaction is, perhaps, brought about by nitric oxide or nitrous acid, but the action of chlorine is not easily explained. The use of bromine or iodine instead of nitric acid in the murexide test for uric acid is recommended as giving more certain results, with less liability to failure from excessive heating. Hypoxanthine, xanthine, theobromine, and caffeine, when subjected to successive oxidation and reduction under the same conditions as uric acid, also yield murexide, and the absorption of iodine by urine is partly due to the presence of the two first-named compounds. It is found, in fact, that the elimination of the uric acid and urates from urine does not wholly obviate the difficulties in the detection of traces of iodides therein.   N. L.

Nitrobiuret and Amidobiuret. By JOHANNES THIELE and EMIL UHLFELDER (*Annalen*, 1898, **303**, 93—107).—*Nitrobiuret*,

$$NO_2 \cdot NH \cdot CO \cdot NH \cdot CO \cdot NH_2,$$
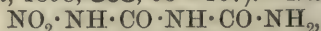
prepared by adding biuret in small portions to a mixture of concentrated nitric and sulphuric acids, separates from water as a white, crystalline powder, which melts and decomposes at 165°; it does not develop colour with alkali and copper sulphate, but gives the nitramine reaction with ferrous sulphate and sulphuric acid, and is resolved by boiling water into carbonic anhydride, nitrous oxide, and carbamide. The *potassium* and *silver* derivatives are anhydrous.

Dinitrobiuret, $NH(CO \cdot NH \cdot NO_2)_2$, produced when the finely divided nitro-derivative is added to fuming nitric acid cooled with a freezing mixture, crystallises from methylic alcohol in white needles, and explodes at 124°; it gives the nitramine reaction, and is resolved into nitrous oxide, carbonic anhydride, and ammonia under the influence of boiling water. The *potassium* derivative crystallises from water in colourless, rhombic plates.

Benzylideneamidobiuret, $CHPh:N \cdot NH \cdot CO \cdot NH \cdot CO \cdot NH_2$, obtained on reducing nitrobiuret, and treating the product with benzaldehyde, crystallises from alcohol in small, white needles, and melts at 202°. Amidobiuret *hydrochloride* is formed when the benzylidene derivative, moistened with alcohol, is heated with concentrated hydrochloric acid on the water-bath; it crystallises from alcohol in plates, and melts at 185°. It dissolves readily in water, and is gradually resolved into ammonium chloride and hydrazodicarbonimide (urazole) when the aqueous solution is boiled; it reduces cold, ammoniacal silver nitrate and hot Fehling's solution. The *nitrate* crystallises from boiling alcohol in beautiful needles, and melts at 165°; it is best prepared by the action of concentrated nitric acid on the *acetone* (β-propylidene) *compound*, $CMe_2:N \cdot NH \cdot CO \cdot NH \cdot CO \cdot NH_2$, which crystallises in white needles and melts at 189°. The *picrate* melts at 175°.

Allophanylhydrazoisobutyronitrile,*

$$CN \cdot CMe_2 \cdot NH \cdot NH \cdot CO \cdot NH \cdot CO \cdot NH_2,$$
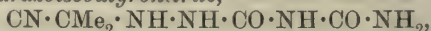
prepared by the action of hydrogen cyanide on the acetone compound of amidobiuret, crystallises in prismatic plates and melts at 146°; oxidation with potassium permanganate converts it into *allophanylazoisobutyronitrile*, $CN \cdot CMe_2 \cdot N:N \cdot CO \cdot NH \cdot CO \cdot NH_2$, which crystallises from benzene in yellow, rhombic plates, and melts and decomposes at 127°.

Allophanazide, $NH_2 \cdot CO \cdot NH \cdot CO \cdot N{<}^{N}_{N}$, obtained by the action of nitrous acid on amidobiuret, melts and decomposes at 195°; it is insoluble in water, but dissolves in aqueous ammonia and in alcohol, undergoing decomposition. Silver nitrate precipitates, from the alcoholic solution, a white, highly explosive substance, which dissolves in ammonia and nitric acid. When the azide is heated with boiling alcohol, diazoimide is eliminated, and ethylic allophanate produced.

Tetruret, $NH(CO \cdot NH \cdot CO \cdot NH_2)_2$, prepared by the action of ammonia on allophanazide, crystallises in colourless, rhombic prisms, and

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* *Allophanyl* is the name given by the authors to the radicle $NH_2 \cdot CO \cdot NH \cdot CO$.

melts at 186°; copper sulphate and alkali develop a deep violet coloration, more intense, but less red than the biuret reaction. M. O. F.

Nitrodicyanodiamidine and Amidodicyanodiamidine. By JOHANNES THIELE and EMIL UHLFELDER (*Annalen*, 1898, **303**, 107—114).—*Nitrodicyanodiamidine*, $NO_2 \cdot NH \cdot CO \cdot NH \cdot C(NH_2)\vdots NH$, prepared by adding dicyanodiamide to a mixture of concentrated nitric and sulphuric acids, forms a microcrystalline powder soluble with difficulty in water and in alcohol; it is neutral in reaction, and when heated with water, becomes alkaline, with elimination of nitrous oxide and carbonic anhydride, guanidine carbonate crystallising from the liquid. The *silver* derivative decrepitates when heated.

Amidodicyanodiamidine *dihydrochloride* forms white needles and melts at 191°; the *picrate* becomes brown at 198°, and melts at 236°. The benzylidene compound forms a *hydrochloride*, which crystallises from alcohol in white prisms and melts at 226°.

Acetoneamidodicyanodiamidine *hydrochloride*,

$$CMe_2\vdots N \cdot NH \cdot CO \cdot NH \cdot C(NH_2)\vdots NH, HCl,$$

crystallises from alcohol in small, white leaflets and needles, and melts at 206°.

Guanidinecarboxylazide *hydrochloride*, $N_3 \cdot CO \cdot NH \cdot C(NH_2)\vdots NH, HCl$, prepared by adding cold, aqueous amidodicyanodiamidine hydrochloride to chloroform saturated with dried nitrous anhydride, melts at 157°, and explodes when heated on platinum foil. Boiling alcohol eliminates diazoimide, and yields the *compound* $C_4H_{10}N_4O_5$, which crystallises in elongated, thin prisms and melts at 187°.

M. O. F.

Chemistry of Acetylene. By GEORG SCHROETER (*Annalen*, 1898, **303**, 114—132. Compare Abstr., 1898, i, 614).—Acetaldehydedisulphonic acid, $COH \cdot CH(SO_3H)_2$, produced by the action of concentrated sulphuric acid on acetylene, has not been obtained crystalline, but forms a syrup which dissolves in alcohol. The *barium* salt contains $2H_2O$, and the *basic barium* salt, which is less readily soluble, crystallises from water in needles containing $4H_2O$; the *potassium* salt contains $1H_2O$, and when treated with potassium hydrogen sulphite, yields the potassium hydrogen sulphite compound of potassium acetaldehydedisulphonate, already obtained by Rathke from chloral and potassium sulphite. The *sodium* salt dissolves in water more freely than the barium and potassium salts, and contains $1H_2O$; the *silver*, *copper*, and *lead* salts are also readily soluble, and the *basic lead* salt contains $1H_2O$.

Acetaldoximedisulphonic acid, $NOH\vdots CH \cdot CH(SO_3H)_2$, forms a *potassium* salt which crystallises from water in lustrous needles containing $1H_2O$. Acetaldehydephenylhydrazonedisulphonic acid,

$$NHPh \cdot N\vdots CH \cdot CH(SO_3H)_2,$$
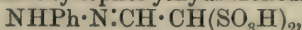
forms a *barium* salt which crystallises from water in leaflets containing $2H_2O$. Acetalazinetetrasulphonic acid, $N_2[\vdots CH \cdot CH(SO_3H)_2]_2$, forms a *barium* salt which contains $6H_2O$; the *hydrazine* salt contains $2H_2O$, and decomposes at 200°.

The *sulphates* of acetaldehydedisulphonic acid,

$$SO_4H \cdot CH(OH) \cdot CH(SO_3H)_2, \text{ and } SO_2[\cdot O \cdot CH(OH) \cdot CH(SO_3H)_2]_2,$$
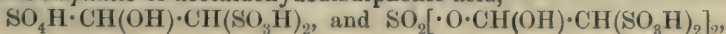
are also produced when fuming sulphuric acid is saturated with
acetylene.   M. O. F.

1 : 2-Acetylfurfuran; and its Occurrence in Wood Tar. By
LOUIS BOUVEAULT (*Compt. rend.*, 1897, **125**, 1184—1186).—This compound is produced synthetically by heating together on the water-
bath ethylic pyromucate and ethylic acetate in the presence of sodium.
The product, after treatment with dilute hydrochloric acid, yields
1 : 2-*ethylic pyromucylacetate*, $C_4OH_3 \cdot CO \cdot CH_2 \cdot COOEt$, which boils at
142—143° under a pressure of 10 mm. and has an odour resembling
that of ethylic acetoacetate.

2-*Acetylfurfuran*, $\begin{matrix} CH : CH \\ CH : CAc \end{matrix} > O$, produced by the hydrolysis of the
preceding compound with 25 per cent. sulphuric acid, boils at 67°
under a pressure of 10 mm., solidifies to a mass of crystals melting
at 29·5°, and has an odour recalling that of acetophenone.

The oil boiling between 150—200°, obtained by the distillation of
beech- and oak-wood after removal of the phenolic and basic substances, is rectified under reduced pressure. The fraction boiling
between 60° and 70° under a pressure of 10 mm. is treated with excess
of hydroxylamine; the product distilled under the same pressure
yields a mixture of oximes boiling at 105—115°. The distillate
yields a crop of crystals melting at 127—128°, and consisting of the
oxime of methylcyclopentenone, C_6H_8O, a compound already obtained
from wood tar. By warming the oxime with acetic anhydride, an
acetyl derivative, $C_6H_8N \cdot OAc$, is produced, which boils at 123° under
a pressure of 10 mm., and crystallises in needles melting at 73°.

The greater portion of the rectified oximes remains liquid, and on
treatment with acetic anhydride yields the *acetyl* derivative of
1 : 2-acetylfurfuranoxime which boils at 135° under a pressure of
10 mm., and crystallises from ether in needles melting at 96°.
1 : 2-*Acetylfurfuranoxime* is obtained by hydrolysing the acetyl compound with alcoholic potash; it boils at 110—111° under a pressure
of 10 mm., and crystallises from ether in well-defined prisms melting
at 104°.

When the oxime is hydrolysed with 25 per cent. sulphuric acid,
1 : 2-acetylfurfuran is regenerated.   G. T. M.

Decomposition of Pyromucates of the Alkaline Earths. By
PAUL FREUNDLER (*Bull. Soc. Chim.*, 1897, [iii], **17**, 609—612).—The
author has prepared furfuran by Limpricht's method (*Annalen*, 1873,
165, 281), namely, by heating barium pyromucate with soda-lime.
It is not advisable to use more than 100 grams of the barium salt at
once, and the yield is extremely poor, only some 4—6 grams ·of
furfuran being obtained from 100 of the barium salt. A considerable
amount of gas is evolved during the reaction, and this consists of equal
volumes of an unsaturated hydrocarbon, C_3H_4 (this vol., i, 98), and of
carbonic oxide, or hydrogen when an excess of soda-lime is employed. No
better yield could be obtained by employing the calcium in place of
the barium salt. Experiments have also been made by heating the
barium salt with barium oxide under reduced pressure, and also by

heating the barium salt alone, both under atmospheric and reduced pressures; the products obtained in all cases were furfuran (10—12 per cent., hydrocarbon, C_3H_4 (5—6 per cent.), carbonic oxide (3—4 per cent.), hydrogen and the ketone, $(C_4H_3O)_2CO$ (1—2 per cent.).

<div style="text-align:right">J. J. S.</div>

A New Series of Cyclic Ketones. By AUGUSTE BÉHAL (*Compt. rend.*, 1897, **125**, 1036—1038).—The heavy oil obtained by the distillation of wood tar consists of a mixture of acidic, basic, and neutral substances; the new ketones are separated from the neutral portions by extraction with concentrated hydrochloric acid, in which they are soluble. The acidic extract, diluted, and subjected to distillation with steam, yields a distillate containing the ketones in the form of a supernatant, yellow oil having an odour of menthol, and boiling between 180° and 205°.

The ketones differ in their solubility in hydrochloric acid, and a partial separation may be effected by the use of various strengths of acid. The greater portion of the mixture is dissolved by a solution of dilute acid (1 : 2), and this portion, when rectified, distils at 190—192°. The ketones in the distillate are converted into oximes, and these into their benzoyl derivatives. The latter can be separated into two distinct substances, the one less soluble in benzene, alcohol, and ether, and melting at 167°, the other far more soluble in these solvents and melting at 128—129°. The oximes are regenerated by the alkaline hydrolysis of the two benzoyl derivatives, that derived from the less soluble benzoyl derivative (m. p. 167°) melting at 121·5°, and that from the more soluble compound (m. p. 129°) at 102·5°.

The parent ketones are obtained by distilling the oximes with 20 per cent. hydrochloric acid. The oxime of higher melting point yields a ketone which boils at 192° under a pressure of 760 mm., and is soluble in water and the ordinary organic solvents. This ketone can be obtained in crystals and melts at 12°; its sp. gr. = 0·9866 at 0°.

Another ketone, which also boils at 192°, is furnished by the oxime of lower melting point; it does not solidify when cooled to − 27°; it is soluble in water and the ordinary organic solvents, and its sp. gr. = 0·9539 at 0°.

The quantity of these ketones in the heavy oil of wood tar amounts to 16 per cent., and they belong chiefly to the tetrahydrobenzene series.

<div style="text-align:right">G. T. M.</div>

Action of Potassium Hydrosulphide on Orthocyanobenzylic Chloride. By SIEGMUND GABRIEL and ERNST LEUPOLD (*Ber.*, 1898, **31**, 2646—2654. Compare Abstr., 1890, 1249).—When orthocyanobenzylic chloride is treated with potassium hydrosulphide, a compound, C_8H_7NS, is produced, which may be regarded either as orthocyanobenzylic mercaptan, $CN \cdot C_6H_4 \cdot CH_2 \cdot SH$, or as thiophthalimidine, $C_6H_4 {<}^{-CH_2-}_{C(NH)} {>} S$. The continued action of potassium hydrosulphide produces *dithiophthalide*, $C_6H_4 {<}^{CH_2}_{CS} {>} S$, which crystallises in reddish, flat plates melting at 68°; this substance again is converted by excess of the sulphide into a sparingly soluble *compound*, $C_{16}H_{10}S_3$, which

crystallises in needles with a green reflex, and probably has the constitution $CH_2 \begin{smallmatrix} S \\ C_6H_4 \end{smallmatrix} C:C \begin{smallmatrix} S \\ C_6H_4 \end{smallmatrix} CS$. On oxidation with nitric acid, this compound is converted into *dithiodiphthalyl*,

$$CO \begin{smallmatrix} S \\ C_6H_4 \end{smallmatrix} C:C \begin{smallmatrix} S \\ C_6H_4 \end{smallmatrix} CO,$$
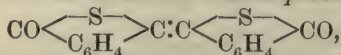
which crystallises in long, greenish-yellow needles, and melts at 332—333° (uncorr.). Fuming nitric acid converts dithiodiphthalyl into diphthalylic acid, $C_{16}H_{10}O_6$, and its constitution is thus established. When this is boiled with alkalis, it yields a salt of the corresponding hydroxy-acid, which is decomposed by acids, with formation of the dilactone. When a solution of dithiodiphthalyl in alcoholic sodium methoxide is treated with methylic iodide, the *tetramethylic* derivative $SMe \cdot CO \cdot C_6H_4 \cdot C(OMe){:}C(OMe) \cdot C_6H_4 \cdot CO \cdot SMe$, of this acid is produced, which crystallises in yellow, six-sided tablets melting at 160—161°; on reduction, this methylic derivative is converted into two isomeric compounds, $C_{16}H_{10}O_4$, one of which is an acid, and the other an indifferent substance. The former crystallises in oblique prisms and melts at 228—229°, whilst the latter forms snow-white needles melting at 255—257°; the constitution of these two compounds is shown by the fact that they are both formed when deoxybenzoinorthodicarboxylic acid, $COOH \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot COOH$, is heated, and are reconverted into this acid when they are heated with alkalis. The indifferent substance is, therefore, an inner anhydride of deoxybenzoindicarboxylic acid, whilst the acid is a lactonic acid, the exact constitution being still uncertain in both cases.

<div style="text-align: right">A. H.</div>

Electrolytic Reduction of the Nitro-group. By WALTHER LÖB (*Zeit. Elektrochem.*, 1898, 4, 428. Compare Abstr., 1897, i, 331; and 1898, i, 14).—The author's object was to isolate intermediate reduction products by adding a substance which will combine with them, and so withdraw them from further reduction. When a mixture of 10 grams of nitrobenzene, 35 grams of fuming hydrochloric acid, 25 c.c. of water, and 70 c.c. of alcohol is placed in a porous cell containing a lead cathode, and this is immersed in dilute sulphuric acid (1 : 10) containing a platinum anode, aniline is practically the only product obtained with E.M.F.'s from 2·5 to 6 volts, and temperature from 20° to 80°. When the 25 c.c. of water is replaced by 25 c.c. of 40 per cent. formaldehyde solution, and the electrolysis conducted with 5 volts and 2 ampères, at 45—60°, a polymeride of paranhydrohydroxylaminobenzylic alcohol, $(OH \cdot CH_2 \cdot C_6H_4 \cdot NH \cdot OH - H_2O)_n$, is obtained. This compound is also formed by the interaction of phenylhydroxylamine and formaldehyde in presence of hydrochloric acid. It is a red, amorphous powder, which yields paraleucaniline with aniline and aniline hydrochloride, whilst with nitrous acid a diazo-derivative is formed which yields parahydroxybenzaldehyde on boiling. Its hydrochloride dissolves in warm, concentrated hydrochloric acid, and the free base is obtained by pouring this solution into dilute ammonia. The base decomposes at high temperatures without melting, may be boiled with caustic soda without decomposition, is insoluble in most

solvents, slightly soluble in chloroform, and more so in aniline and concentrated sulphuric acid.

When the electrolysis is carried out with 2·8—3 volts at 30°, methylenediparanhydroamidobenzylic alcohol,

$$CH_2 \begin{cases} HN \cdot C_6H_4 \cdot CH_2 \\ HN \cdot C_6H_4 \cdot CH_2 \end{cases} O,$$
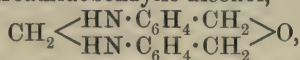
is the only product. This substance has not previously been described, and may be obtained by the direct interaction of aniline and formaldehyde. The hydrochloride and platinochloride were analysed. The base is a pale yellow, amorphous powder, soluble in dilute acids, chloroform, and aniline, less soluble in alcohol and glacial acetic acid, insoluble in water, ether, alkalis, and light petroleum. Its solutions in acids are yellow or red.

When nitrobenzene (10 grams), 40 per cent. formaldehyde (10 grams), alcohol (10 grams), and fuming hydrochloric acid (35 grams) are gradually treated with zinc dust (20 grams) at 50°, paranhydrohydroxylaminobenzylic alcohol is formed almost quantitatively.

In order to prevent the reaction of the formaldehyde with the hydrogen atom in the para-position to the nitro-group, experiments were tried with paranitrotoluene.

Paranitrotoluene (10 grams), alcohol (100 c.c.), water (4 c.c.), and sodium hydroxide (5 grams) were electrolysed as above described with 1·3 ampères and 5—6 volts. A quantitative yield of parazotoluene was obtained.

Paranitrotoluene (10 grams), suspended in fuming hydrochloric acid (100 c.c.), and electrolysed with 5 volts and 1·7 ampères, gave a quantitative yield of paratoluidine.

Paranitrotoluene (10 grams), alcohol (80 c.c.), water (35 c.c.), and fuming hydrochloric acid (35 grams) electrolysed with 1·5 ampères and 4 volts, also gave an almost quantitative yield of paratoluidine. In the last case, when the water was replaced by 40 per cent. formaldehyde, two substances were obtained in nearly equal quantities, namely, paradimethyltoluidine and paradimethyleneditoluidine,

$$C_6H_4Me \cdot N \begin{cases} CH_2 \\ CH_2 \end{cases} N \cdot C_6H_4Me.$$
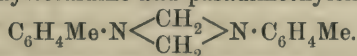
The latter is formed almost quantitatively by the action of formaldehyde on paratoluidine in acid solution, and crystallises from dilute alcohol in slender needles melting at from 119—125°; it cannot be reduced, either chemically or electrolytically, to paradimethyltoluidine, except in presence of formaldehyde, when the reduction proceeds perfectly smoothly, yielding paradimethyltoluidine and paratoluidine.　　　　　　　　　　　　　　　　　　　　　T. E.

Reduction of 2-Nitro-3:5-dimethylphenylnitromethane [ω-2-Dinitromesitylene]. By EUGEN BAMBERGER and MAX WEILER (*J. pr. Chem.*, 1898, [ii], **58**, 333—361).—When ω-2-dinitromesitylene, $NO_2 \cdot C_6H_2Me_2 \cdot CH_2 \cdot NO_2$ (Konowaloff, Abstr., 1896, i, 674), is dissolved in 95 per cent. alcohol, and reduced with 4 per cent. sodium amalgam at − 10°, 2-*amido*-3:5-*dimethylbenzaldoxime*, $NH_2 \cdot C_6H_2Me_2 \cdot CH:NOH$, is formed; this melts at 170—171°, dissolves in dilute mineral acids and caustic alkalis, forms a *dibenzoyl* derivative melting at 142—142·5°,

and a yellow *compound* melting at 179—180°, when mixed with meta-nitrobenzaldehyde in dilute hydrochloric acid solution. When boiled with dilute sulphuric acid, it yields 1-*amido*-3 : 5-*dimethylbenzaldehyde*, $NH_2 \cdot C_6H_2Me_2 \cdot CHO$, identical with a product obtained from mesitylene in the manner described below ; this is yellow, and melts at 48—49° ; with phenylhydrazine, it yields a *substance* melting at 142—143°, and possibly not a normal hydrazone, as it is not soluble in acids. When the oxime is boiled for a short time with acetic anhydride, it forms 2-*acetamidomesitylenonitrile*, $NHAc \cdot C_6H_2Me_2 \cdot CN$, together with a substance that melts at about 150° ; the nitrile melts at 196·5—197·5°, and is insoluble in dilute acids and alkalis, but when warmed with these it is converted into a substance that melts at 271·5—272·5° ; the latter has the properties of a quinazolone (Weddigè, Abstr., 1885, 661 ; 1887, 1044), and must, therefore, be *trimethylquinazolone*,

$$C_6H_2Me_2 \begin{array}{c} CO \cdot NH \\ \diagdown \ \ \ | \\ N = CMe \end{array}$$; its orange-yellow platinochloride is still un-

melted at 345°. When the oxime is dissolved in a mixture of acetic acid and anhydride, and the mixture is saturated with gaseous hydrogen chloride at 0° and allowed to remain (Beckmann's mixture), the product, which melts at 166·5—168°, has the properties of an acetylisindazole (Auwers, Abstr., 1892, 186 ; 1896, i, 504), and con-

sequently must be *acetyldimethylisindazole*, $C_6H_2Me_2 \begin{array}{c} CH \\ \diagdown \ \diagup \\ NAc \end{array} N$; it is

soluble in cold, dilute hydrochloric acid, but not in cold, aqueous caustic potash ; when boiled with the latter, it dissolves gradually, and from the solution acetic acid precipitates a substance melting at 191·5—192·5°, which possibly may be 2-acetamido-3 : 5-dimethyl-benzaldoxime. When the amidodimethylbenzaldoxime is diazotised in hydrochloric acid solution with sodium nitrite, the product is

dimethylindiazone oxime, $C_6H_2Me_2 \begin{array}{c} C(NOH) \\ \diagdown \ \ \ \ \ \diagup \\ N \end{array} N$; this is yellow, melts

and decomposes at 181·5—182·5°, and dissolves in cold, dilute mineral acids and alkalis, but is decomposed by these on boiling, the products being, when acid is used, hydroxylamine ; amidodimethylbenzaldehyde (see above) ; *dimethylsalicylaldehyde*, which solidifies at about 15°, and forms an *oxime*, $OH \cdot C_6H_2Me_2 \cdot CH:NOH$, melting at 138·5—139·5° ; and a substance which forms an *oxime* melting at 99—100·5° and is devoid of acid character.

If ω-2-dinitromesitylene is dissolved in commercial *absolute* alcohol and reduced with 4 per cent. sodium amalgam at −5° to 0°, the products then obtained are a resin ; mesitylenic acid ; amidodimethylbenz-aldoxime ; a *base*, $(C_9H_{12}NO)_x$, possibly $C_2H_2(OH)_2(C_6H_2Me_2 \cdot NH_2)_2$, which melts at 260° ; another *base*, or mixture of bases, which melts at 133—147·5°, and has the composition C, 70·2—72·0 ; H, 8·26—8·51 ; N, 9·15 (these last two bases are insoluble in alkalis) ; and a small quantity of an *acid* containing nitrogen.

2-Amido-3 : 5-dimethylbenzaldehyde was prepared from mesitylene by oxidising it to bimethylbenzaldehyde with chromyl chloride in carbon bisulphide solution ; or, better, by converting it into mesitylic bromide and oxidising this with chromate or lead nitrate, nitrating the aldehyde with a solution of potassium nitrate in strong sulphuric

acid cooled by a freezing mixture, and reducing the 2-*nitro*-3 : 5-*di-methylbenzaldehyde*, $NO_2 \cdot C_6H_2Me_2 \cdot CHO$, which melts at 102—103°, with ferrous sulphate and ammonia. C. F. B.

Hydrolysis of Ethanedicatechol [Dicatechol Acetylenic Ether]. By CHARLES MOUREU (*Compt. rend.*, 1898, 127, 276—278).— The compound $C_8H_8O_4$, obtained by boiling dicatechol acetylenic ether with dilute sulphuric acid, is *orthohydroxyphenoxyacetic acid*, $OH \cdot C_6H_4 \cdot O \cdot CH_2 \cdot COOH$. It is acid to litmus, phenolphthalein, methyl-orange, and the blue—C4B, gives an intense blue coloration with ferric chloride, and reduces ammoniacal silver nitrate in the cold, but gives no coloration with rosaniline hydrogen sulphite. Its phenyl-hydrazone crystallises in white, rectangular scales which melt and decompose at 193°. When heated, it forms a lactone which crystal-lises in large, elongated prisms melting at 54—56°, and when boiled with water is reconverted into the acid melting at 130—131°.

The same acid is obtained by heating sodium monochloracetate with monosodium catechol and treating the product with hydrochloric acid.

It is probable that when the dicatechol acetylenic ether is boiled with the dilute acid, the first product is a compound, $C_6H_4 \! : \! O_2 \! : \! CH \cdot CHO$, which, by hydration, is converted into $OH \cdot C_6H_4 \cdot O \cdot CH(OH) \cdot CHO$, and the latter, being unstable, changes by intramolecular migration of an oxygen atom into the acid $OH \cdot C_6H_4 \cdot O \cdot CH_2 \cdot COOH$. C. H. B.

Preparation of Paraquinones from Indophenols. By PIERRE H. BAYRAC (*Ann. Chim. Phys.*, 1897, [vii], 10, 18—79).—This paper gives full details of work which has already been published (see Abstr., 1895, i, 412, 416 ; 1896, i, 605, 606). G. T. M.

Formation of Chains. XXVII. Benzylaniline. XXVIII. Diphenylamine. By CARL A. BISCHOFF (*Ber.*, 1898, 31, 2672—2677, 2678—2683. Compare Abstr., 1898, i, 182).—Chain formation occurs less readily in the case of benzylaniline and of diphenylamine than with the secondary bases discussed in the preceding papers ; this is indicated by the numbers in the following table, which give the approxi-mate extent in percentages of the theoretical maximum to which action takes place between the amines and ethylic salts there tabulated.

Ethylic salt.	Benzylaniline.			Diphenylamine.				
	At 100°.	At 110°.	At 120°.	At 100°.	At 110°.	At 120°.	At 170—175°.	At 195—200°.
Bromopropionate...	Nil	29·2	50·9		Nil	36·1	33·5	55·8
Bromophenyl-acetate	40·3			27·0			42·0	
Bromobutyrate......			14·0			4·4	8·3	
Bromisobutyrate ...			Nil			9·1		
Bromisovalerate ...			Nil			3·0		

The following new substances were prepared in the course of the investigation.

Phenylbenzylglycine, $CH_2Ph \cdot NPh \cdot CH_2 \cdot COOH$, prepared from

benzylaniline, chloracetic acid, and sodium acetate, crystallises from alcohol in needles, and melts at $121-123°$; it decomposes on exposure to light and air, when an intense odour of benzaldehyde becomes perceptible.

a-*Bromopropionobenzylanilide*, $CH_2Ph \cdot NPh \cdot CO \cdot CHMeBr$, formed by the action of a-bromopropionic bromide on benzylaniline, separates from alcohol in crystals belonging to the rhombic system and melts at $78°$. a-*Bromobutyrobenzylanilide*, $CH_2Ph \cdot NPh \cdot CO \cdot CHEtBr$, is deposited by dilute alcohol in colourless crystals and melts at $50-54°$; a-*bromisobutyrobenzylanilide*, $CH_2Ph \cdot NPh \cdot CO \cdot CMe_2Br$, is an oil. a-*Bromisovalerobenzylanilide*, $CH_2Ph \cdot NPh \cdot CO \cdot CHBr \cdot CHMe_2$, crystallises from 96 per cent. alcohol in aggregates of colourless prisms and melts at $95-96°$.

a-*Bromopropionodiphenylamide*, $NPh_2 \cdot CO \cdot CHMeBr$, separates from hot alcohol in colourless, transparent crystals belonging to the monoclinic system and melts at $109°$. a-*Bromobutyrodiphenylamide*,

$$NPh_2 \cdot CO \cdot CHEtBr,$$
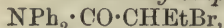
is deposited by alcohol in large, lustrous crystals and melts at $85°$ a-*Bromisobutyrodiphenylamide*, $NPh_2 \cdot CO \cdot CMe_2Br$, crystallises from alcohol in plates, and melts at $82°$. a-*Bromisovalerodiphenylamide*, $NPh_2 \cdot CO \cdot CHBr \cdot CHMe_2$, crystallises in colourless, four-sided plates, and melts at $110·5°$.   M. O. F.

Peracetylation of Phenacetine. By AUGUSTIN BISTRZYCKI and FRITZ ULFFERS (*Ber.*, 1898, 31, 2788—2790. Compare Abstr., 1894, i, 181, and Kay, *ibid.*, 77).—Phenacetine, $OEt \cdot C_6H_4 \cdot NHAc$, is boiled for several hours with a large excess of acetic anhydride in a reflux apparatus, moisture being excluded by means of a calcium chloride tube; the acetic acid formed and some of the anhydride is distilled over; the residue is boiled again with more acetic anhydride, the product distilled under 15 mm. pressure in an oil bath at $180°$, and the residue poured out. In this way, *diacetophenetidide*, $OEt \cdot C_6H_4 \cdot NAc_2$, is obtained; it melts at $53·5-54°$, and boils at $182°$ under a pressure of 12 mm.; when kept in stoppered bottles, it is decomposed very slowly by the moisture of the air, acetic acid being formed; its physiological action is similar to that of phenacetine, and the same effect is sometimes obtained, although it is commonly less lasting, with a smaller dose, than in the case of phenacetine.

C. F. B.

Potassiodiphenylamine. By CARL HÄUSSERMANN (*J. pr. Chem.*, 1898, [ii] 58, 367—368).—Diphenylamine (30 parts) is melted in a strong, round-bottomed flask in a boiling water-bath, potassium (1 part) is added little by little, and as soon as the violent action has ceased, the flask is exhausted of air and the heating is continued for 3—4 hours until the potassium has disappeared, after which unchanged diphenylamine is removed by digestion with absolute ether. The product, presumably NPh_2K, is a yellow, sandy powder, which absorbs oxygen from the air, turning black, and unites with dry carbonic anhydride to form *potassium diphenylthiocarbamate*, $NPh_2 \cdot COOK$, a white powder which is decomposed by water into diphenylamine and potassium hydrogen carbonate.   C. F. B.

Nitroso-derivatives of Aromatic Amines. By CAMILLE MATIGNON and DELIGNY (*Compt. rend.*, 1897, **125**, 1103—1105).—The authors have made a comparative study of the heats of combustion of the following nitroso-compounds of aromatic amines: diphenylnitrosamine, nitrosophenylaniline, and paranitrosodimethylaniline. They find that the introduction of a nitroso-group into the aromatic nucleus lowers the heat of combustion by 15 calories, whereas its attachment to the nitrogen of the side-chain lowers this by 9·8 calories. This difference explains the readiness with which the nitroso-group migrates from the nitrogen atom into the nucleus. Provided that the molecules originally contain a sufficient number of atoms, the introduction of a new radicle produces the same change in the heats of combustion if the entering group becomes similarly attached in each case. G. T. M.

Behaviour of Substituted Amidonitriles towards Aromatic Aldehydes in Presence of Alkali. By WILHELM VON MILLER and JOSEF PLÖCHL (*Ber.*, 1898, **31**, 2699—2717).—Substituted amidonitriles yield alkylideneamides with aromatic aldehydes, just as they give rise to amides under the influence of water.

[With BR. BRUHN.]—The *compound* $C_{21}H_{18}N_2O$, obtained by the action of benzaldehyde on benzylideneaniline under the influence of alcoholic potassium cyanide, is also produced gradually in absence of benzaldehyde; it crystallises from amylic alcohol or nitrobenzene in microscopic needles and melts at 249°. The *isomeride*, formed at the same time, crystallises from alcohol in pale yellow prisms melting at 208°; it is accompanied by a small quantity of a substance which crystallises in pink leaflets and melts at 151°. The *compound* $C_{22}H_{20}N_2O_3$ is also produced; it melts and decomposes at 194° and is distinctly acidic in character. The three compounds are formed when alcoholic potassium cyanide acts on the nitrile of phenylanilidoacetic acid and benzaldehyde, and they are all resolved into benzaldehyde, ammonia, and phenylanilidoacetic acid under the influence of boiling dilute hydrochloric acid. The less readily fusible isomeride is converted into that melting at 208° by the action of boiling alcoholic potash, and of boiling glacial acetic acid; the action in each case is reversible.

[With LUDWIG GERNGROSS.]—From phenylanilidoacetonitrile and cuminaldehyde dissolved in alcoholic potash, two indifferent, isomeric *compounds*, $C_{24}H_{24}N_2O$, are obtained melting at 226° and 198° respectively; they are also produced by the action of cuminaldehyde on benzylideneaniline, along with an acidic *compound*, $C_{25}H_{26}N_2O_3$, and the *nitrile*, $C_{25}H_{25}N_3O$, which melt at 208° and 256° respectively. The indifferent compounds are interconvertible, and, like the acid, yield cuminaldehyde, ammonia, and phenylanilidoacetic acid with boiling hydrochloric acid; phenylhydrazine gives rise to cuminphenylhydrazone.

Cumenylanilidoacetonitrile, $C_{17}H_{18}N_2$, from cumylideneaniline and hydrogen cyanide, crystallises from alcohol in lustrous, monoclinic prisms and melts at 86°. *Cumenylanilidoacetamide*, $C_{17}H_{20}N_2O$, obtained by the action of concentrated sulphuric acid on the nitrile, forms colourless prisms melting at 159°, and yields a *nitroso*-deriva-

tive which melts at 132°. *Cumenylanilidoacetic acid*, $C_{17}H_{19}NO_2$, crystallises in small aggregates of needles; it melts and decomposes at 158°.

[With P. Scheitz.]—*Benzylideneparanisidine*, $C_{14}H_{13}NO$, crystallises in leaflets and melts at 72°; hydrogen cyanide converts it into the *nitrile* of phenylparanisidoacetic acid, which melts at 85°, whilst the *amide* melts at 120°. *Phenylparanisidoacetic acid*, $C_{15}H_{15}NO_3$, melts and decomposes at 184°. The two indifferent *compounds*, $C_{22}H_{20}N_2O_2$, obtained from the nitrile with benzaldehyde and alcoholic potash, melt at 222° and 193° respectively; the acidic *compound*, $C_{23}H_{22}N_2O_4$, melts at 198°, with effervescence, and the corresponding *nitrile*, $C_{23}H_{21}N_3O_2$, melts at 233°.

[With R. Luppe.]—Anhydroformaldehydeaniline with benzaldehyde and potassium cyanide, or anilidoacetonitrile with benzaldehyde and alcoholic potash, yields two indifferent *compounds*, $C_{15}H_{14}N_2O$, melting at 219° and 169° respectively, along with an acidic *compound*, $C_{16}H_{16}N_2O_3$, which melts and effervesces at 239°; when the compound melting at 169° is recrystallised from alcohol, it is in part converted into the isomeride, the change being complete on exposing the substance to a temperature of 170° during some hours. Boiling 20 per cent. hydrochloric acid resolves the substance into benzaldehyde, ammonia, and anilidoacetic acid.

[With Wilhelm Sieber.]—The indifferent *compounds*, $C_{16}H_{16}N_2O$, obtained from anhydroformaldehydeparatoluidine with benzaldehyde and potassium cyanide, melt at 245° and 168° respectively; the acidic *compound*, $C_{17}H_{18}N_2O_3$, melts at 228°. *Paratoluidoacetic acid*, $C_6H_4Me\cdot NH\cdot CH_2\cdot COOH$, obtained by hydrolysing with 20 per cent. hydrochloric acid the compound which melts at 245°, crystallises from light petroleum in large, lustrous, monoclinic plates, and melts at 132° (compare Bischoff and Hausdörfer, Abstr., 1892, 1335); the *nitrile* melts and decomposes at 61°, and the *amide*, which melts at 168°, yields a *nitroso*-derivative melting at 158°.

[With J. Hamburger].—Ethylideneaniline, with benzaldehyde and potassium cyanide, yields an indifferent *compound*, $C_{16}H_{16}N_2O$, which melts at 203°, and an acidic *compound*, $C_{17}H_{18}N_2O_3$, melting at 220°.

[With W. Kollegorsky.]—Benzylidenemethylamine, with benzaldehyde and potassium cyanide, yields an indifferent *compound*, $C_{16}H_{16}N_2O$, which melts at 152°, and an acidic *compound*, $C_{17}H_{18}N_2O_3$, melting at 179°. Hydrolysis resolves these substances into benzaldehyde, ammonia, and phenylsarcosine. M. O. F.

Stereochemistry of Quinoneoximes. By Friedrich Kehrmann (*Annalen*, 1898, **303**, 1—33. Compare Abstr., 1894, i, 460).—The two modifications in which both the benzoyl and methyl derivatives of metachloroquinoneoxime are produced have been regarded by the author (*loc. cit.*) as stereoisomerides; further evidence in support of this view has been derived from a determination of the molecular weight of the two isomeric acetyl derivatives, and from an examination of the behaviour of parachlorotoluquinone towards hydroxylamine hydrochloride. It being exceptional for the meta-halogen derivatives of toluquinone to yield isomeric oximes, the author concludes that it

is only in the case of a slight difference in the stability of the two forms that the phenomenon is noticeable; when the difference is great, one form only is produced.

[With HUGO GRAB.]—The stable modification of the *acetyl* derivative of metachloroquinoneoxime crystallises from benzene in amber-coloured, four-sided prisms, and melts at 166—167°; the labile *compound* dissolves more readily in benzene, from which it crystallises in yellow leaflets, and melts at 136—137°. Both forms give normal figures for the molecular weight in glacial acetic acid, and yield 4 : 6 : 2-chlorodinitrophenol and 6 : 4-chloramidophenol on oxidation with nitric acid, and on reduction with stannous chloride and hydrochloric acid respectively. The isomerism consequently meets with explanation on the hypothesis of Hantzsch and Werner.

When metachloroquinoneoxime is heated with alcoholic hydroxylamine hydrochloride in a reflux apparatus, it yields metachloroquinonedioxime; the *diacetyl* derivative of this substance occurs only in one modification, which crystallises from benzene in colourless prisms and melts at 171—172°. Oxidation and reduction of the dioxime lead to 1 : 3 : 6-chlorodinitrobenzene and 2 : 1 : 4-chlorodiamidobenzene respectively.

Paradichloroquinoneoxime, $C_6H_3ClNO_2$, separates from benzene in two crystalline forms, and melts indefinitely at 155—160°; it is uncertain whether the difference in crystalline structure represents stereoisomerism. The *acetyl* derivative crystallises from benzene in amber-coloured prisms, and melts at 149°.

[With MICH. TICHVINSKY.]—The *oxime* of 4-chlorotoluquinone occurs in two modifications, which are separated by a method described in the original paper. The more sparingly soluble isomeride crystallises from alcohol in lustrous, brownish-yellow prisms, and decomposes at 170°; the *acetyl* derivative melts at 158—159°. The more readily soluble modification crystallises from alcohol and from toluene in aggregates of slender, pale yellow needles, and decomposes at about 165°; the *acetyl* derivative crystallises in long needles from the benzene mother liquor of the isomeride, and melts at 141—142°.

Chloramidocresol [Me : NH_2 : Cl : OH = 1 : 2 : 4 : 5], obtained by reducing either modification of the oxime with stannous chloride and hydrochloric acid, forms colourless leaflets and melts at 204—205°; the *diacetyl* derivative crystallises from benzene in colourless needles and melts at 162°.

Chlorodinitrocresol [Me : $(NO_2)_2$: Cl : OH = 1 : 2 : 6 : 4 : 5], produced by the action of dilute nitric acid on either modification of the oxime, crystallises from alcohol in yellow leaflets and melts at 108°.

[With CARL RÜST.]—4-*Bromotoluquinone* [Me : O_2 : Br = 1 : 2 : 5 : 4], prepared by treating toluquinone with fuming hydrogen bromide and oxidation of the product with chromic acid, crystallises from alcohol in large, yellow plates and melts at 105°. The *oxime* occurs in two modifications, the more sparingly soluble forming brownish-yellow needles which decompose at 186°, whilst the more readily soluble crystallises from toluene in slender, pale yellow needles and decomposes at 178—180°; the *acetyl* derivatives melt at 166—167° and 131—132° respectively. The corresponding *benzylic ethers* melt at

95—96° and 80—81° respectively; the latter crystallises in the asymmetric system, and has the axial ratio $a : b : c = 1\cdot7562 : 1 : 1\cdot1580$.

Bromamidometacresol [Me : NH$_2$: Br : OH = 1 : 2 : 4 : 5], prepared by reducing either oxime, forms silvery leaflets, and decomposes at 205—208°; the *diacetyl* derivative crystallises from toluene in colourless prisms and melts at 171—172°.

Bromodinitrometacresol [Me : (NO$_2$)$_2$: Br : OH = 1 : 2 : 6 : 4 : 5], obtained from both modifications of the oxime by the action of moderately concentrated nitric acid on the water-bath, crystallises from petroleum in sulphur-yellow octahedra and melts at 115—116°; trinitrocresol, which melts at 106—107°, is produced along with it.

M. O. F.

Ethers of Toluquinoneoxime and their Bearing on the Space-isomerism of Nitrogen. By JOHN L. BRIDGE and WILLIAM C. MORGAN (*Amer. Chem. J.*, 1898, **20**, 761—776).—Toluquinoneorthoxime, which is readily prepared by the action of nitrous acid on metacresol, melts at 155°, not at 145—150°, as stated by Beilstein; toluquinonemetoxime, prepared similarly from orthocresol, melts at 134°. The *silver* derivative, C$_7$H$_6$NO$_2$Ag, of the metoxime, when freshly prepared, is a light reddish-brown powder, which slowly decomposes on exposure to the air, and when thoroughly dry ignites spontaneously on being heated above 60°; when shaken with methylic iodide dissolved in light petroleum, it is partially converted into the corresponding *methyl* derivative, C$_8$H$_9$NO$_2$; this can be better obtained, however, by adding the calculated quantity of methoxylamine hydrochloride to toluquinone dissolved in a large quantity of water. The product in either case, after being recrystallised several times from light petroleum, melts indefinitely between 55° and 70°, and appears to consist of a mixture of two stereoisomerides; *one* more sparingly soluble in light petroleum, can be isolated by fractional crystallisation and melts at 73—74°, but the second modification cannot be separated. The corresponding *acetyl* derivative, C$_9$H$_9$NO$_3$, formed in small quantity on adding acetic chloride to the silver derivative suspended in ether or light petroleum, is resolved by fractional crystallisation from the latter into two stereoisomerides; one of these melts at 112—113°, and crystallises in thick prisms, whilst the other forms spherical aggregates of minute crystals and melts at 85—87°. The *benzoyl* derivative, C$_{14}$H$_{11}$NO$_3$, prepared by acting on the sodium salt of toluquinonemetoxime prepared from orthocresol, is identical with that obtained from the oxime prepared from toluquinone and hydroxylamine hydrochloride; both products are mixtures of two stereoisomerides, one crystallising in bright yellow needles and melting at 193°, the other separating in thick prisms, and melting probably at 142—144°, although fractions were obtained melting at 129°. No trace of the orthoxime could be detected in the product obtained from toluquinone. On adding bromine to a chloroform solution of the benzoate of the metoxime, the *dibromide*, C$_{14}$H$_{11}$Br$_2$NO$_3$, is obtained; it crystallises from glacial acetic acid in white prisms, melts and decomposes at 165°, and is converted by boiling alcohol into a mixture of two stereoisomeric *benzoates*, C$_{14}$H$_{10}$BrNO$_3$, of bromotoluquinonemetoxime; the crude

product melts and decomposes at 155—170°, but after fractional crystallisation from alcohol melts and decomposes at 174°.

The *silver* derivative, $C_7H_6NO_2Ag$, of toluquinoneorthoxime closely resembles the corresponding meta-derivative, but is much more stable than the latter. The *methyl* derivative, $C_8H_9NO_2$, obtained from it crystallises from light petroleum in long needles, melts at 69°, and appears to exist only in one form; when the calculated quantity of bromine is added to its solution in chloroform, the *dibromide*, $C_8H_9Br_2NO_2$, is obtained which crystallises from light petroleum in white prisms and melts at 112°. The same acetyl derivative as was prepared by Wurster and Riedel (Abstr., 1880, 109) from acetic anhydride and toluquinoneorthoxime is formed in small quantity by acting on the silver derivative of the latter with acetic chloride. The corresponding *benzoyl* derivative, $C_{14}H_{11}NO_3$, crystallises from alcohol in flat, brownish-yellow prisms, and melts and partially decomposes at 177°; the *dibromide*, $C_{14}H_{11}Br_2NO_3$, crystallises from glacial acetic acid in stunted orthorhombic prisms, and melts and decomposes at 159°.

In discussing his results, the author emphasises the fact that, whereas the preparation of derivatives of toluquinonemetoxime gives rise to two stereoisomerides, the corresponding derivatives of the orthoxime exist only in one form; it is suggested, as a possible explanation, either that, in the latter case, the proximity of the side-chains prevents the formation of a space-isomeride, or that isomeric substances exist which cannot be distinguished by the ordinary methods. Since no trace of the orthoxime is formed on treating toluquinone with hydroxylamine hydrochloride, Kehrmann's rule (Abstr., 1889, 243) concerning the influence of side-chains in quinones on the position taken by the entering isonitroso-group is confirmed; the latter's views of the space-isomerism of the quinoneoximes also explain the existence of stereoisomeric modifications in the cases dealt with above. W. A. D.

Beckmann's Transformation. By KARL AUWERS and H. CZERNY (*Ber.*, 1898, **31**, 2692—2698).—The production of indazole derivatives by the action of glacial acetic acid with acetic anhydride and hydrogen chloride on the oximes of aromatic orthamidoketones (compare Auwers, Abstr., 1896, i, 503), suggested the possibility of obtaining analogous indoxazenes, $C_6H_4{<}^{CR}_{-O}{>}N$, from the oximes of aromatic orthohydroxyketones. Contrary to expectation, however, the oxime of unsymmetrical orthohydroxymetamethylbenzophenone,

$$OH \cdot C_6H_3Me \cdot CPh \vdots NOH,$$
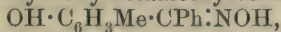
undergoes the Beckmann transformation, yielding benzenyl-3-amido-paracresol, $C_6H_3Me{<}^N_O{>}CPh$, and the anilide of 4-hydroxymeta-toluic acid. In addition to Beckmann's mixture, zinc chloride, phosphorus pentachloride, phosphoric anhydride, and anhydrous copper sulphate induce this change, which also occurs when the substance is distilled under ordinary and reduced pressures; the action of copper sulphate gains in interest from the fact that it has, hitherto, been

employed when transformation of an oxime is to be avoided.   The result of heating the oxime of orthohydroxymetamethylbenzophenone gives support to Beckmann's opinion that the transformation of oximes into amides is an instance of catalytic action (Abstr., 1894, i, 240).

The *oxime* of unsymmetrical orthohydroxymetamethylbenzophenone, $OH \cdot C_6H_3Me \cdot CPh \colon NOH$, crystallises from glacial acetic acid in small, white needles, and melts at 126—128·5°.

Benzenyl-3-amidoparacresol, $C_6H_3Me{<}{\stackrel{N}{O}}{>}CPh$, obtained by the action of Beckmann's mixture, melts at 104°; concentrated hydrochloric acid at 150—160° converts it into benzoic acid and 3-amidoparacresol.   The *dibenzoyl* derivative of 3-amidoparacresol,
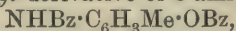
$$NHBz \cdot C_6H_3Me \cdot OBz,$$

crystallises from alcohol in white leaflets and melts at 190—191°; hydrochloric acid precipitates from the solution in caustic soda the *benzoyl* derivative, $NHBz \cdot C_6H_3Me \cdot OH$, which crystallises in nacreous leaflets and melts at 191°.   When either of these compounds is boiled during a few minutes, it yields benzenyl-3-amidoparacresol.

The anilide of 4-hydroxymetatoluic acid, obtained by the action of zinc chloride on the oxime of orthohydroxymetamethylbenzophenone, melts at 158—159°, and not at 53°, as stated by Bargioni; the *hydrogen phosphate* melts at 187—189°.   M. O. F.

Action of Alkylic Salts of β-Ketonic Acids on Paraphene-tidine.   By ERNESTO FOGLINO (*Chem. Centr.*, 1898, i, 501; from *Ann. Chim. Farm.*, 26, 535—541).—By the action of paraphenetidine on ethylic benzoylacetate at 120—130°, alcohol and benzoylacetophene-tidine, $OEt \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_2Bz$, are formed; the latter crystallises from alcohol in white needles, melts at 139—140°, and is insoluble in cold water.   With the ethylic salts of acetoacetic, methylacetoacetic, diethylacetoacetic, benzoylacetoacetic, and acetylsuccinic acids, para-phenetidine at 140—150° yields alcohol, a ketone, and Wenghöfer's paradiphenetoilcarbamide, $CO(NH \cdot C_6H_4 \cdot OEt)_2$.   The last compound is also formed by the action of benzoylacetoacetamide on paraphene-tidine.   E. W. W.

Action of Piperidine on Carbonates Derived from Phenols: Formation of Aromatic Urethanes.   By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1897, 125, 1107—1109).—When piperidine acts on carbonates derived from phenols, urethanes alone are produced, there is no formation of carbamide derivatives.

Piperidine and phenylic carbonate, when simply mixed together, form a *urethane*, $C_5H_{10}N \cdot COOPh$, which melts at 80°, and dissolves in the ordinary organic solvents; it is hydrolysed by caustic potash into phenol and piperidine.

The *urethane*, $C_5H_{10}N \cdot COO \cdot C_6H_4 \cdot OMe$, from guaiacol carbonate and piperidine, crystallises from alcohol in white prisms, melts at 44°, and boils at about 330°.

The corresponding *β-naphthylic urethane*, produced by mixing together β-naphthylic carbonate and piperidine, crystallises in needles and melts

at 107°. The α-naphthylic compound has not yet been obtained crystalline.

When treated with concentrated sulphuric acid, these urethanes yield piperidine sulphate and a sulphonic acid of the corresponding phenolic compound. G. T. M.

Aromatic Urethanes of Conicine. By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1898, **126**, 481—483. Compare preceding abstract).—Conicine and phenylic carbonate, when heated together for 1 hour, form the *urethane*, $C_8H_{16}N \cdot COOPh$, a viscous liquid boiling at 325°; its rotation in alcoholic solution is $[\alpha]_j + 3 \cdot 66°$.

The *urethane*, $C_8H_{16}N \cdot COO \cdot C_6H_4 \cdot OMe$, is obtained in similar manner from guaiacol carbonate; it forms a viscous liquid boiling at 277°. The α- and *β-naphthyl urethanes*, $C_8H_{16}N \cdot COO \cdot C_{10}H_7$, are very viscous liquids boiling above 300°.

All these substances are hydrolysed by caustic potash at 150°, and are decomposed by concentrated sulphuric acid with evolution of carbonic anhydride. G. T. M.

Pseudophthalimidine and Orthocyanobenzylamine. By SIEGMUND GABRIEL and WILLY LANDSBERGER (*Ber.*, 1898, **31**, 2732—2740). —Kiel (*Inaug. Diss. Bonn.*, 1896) has shown that pseudophthalimidine probably has the constitution, $NH\!:\!C\!<^{C_6H_4}_{O}\!>\!CH_2$, which was formerly assigned by Graebe to phthalimidine. The authors have examined the molecular weights of these compounds in order to ascertain whether they both correspond with this formula. Pseudophthalimidine itself is not adapted for this purpose, since it cannot be purified by distillation, and the corresponding nitro-derivative was, therefore, substituted for it.

Orthocyanobenzylic chloride is converted by nitration into 5-*nitro-2-cyanobenzylic chloride*, $CH_2Cl \cdot C_6H_3(NO_2) \cdot CN$, which forms yellowish crystals and melts at 94°. When heated with hydrochloric and acetic acids at 140—150°, it is converted into 5-nitrophthalide, a reaction which indicates the constitution of the compound. The nitro-compound can readily be converted by hydrolysis with sulphuric acid into ω-*chloro-5-nitro-orthotoluamide*,
$$CH_2Cl \cdot C_6H_3(NO_2) \cdot CO \cdot NH_2,$$
which crystallises in matted, snow-white needles melting at 228° when rapidly heated. When heated for some time at 110°, it is converted into 5-*nitropseudophthalimidine*, $NO_2 \cdot C_6H_3\!<^{CH_2}_{C(NH)}\!>\!O$, which crystallises in needles melting at 158°. The *hydrochloride* decomposes in aqueous solution, forming ammonium chloride and nitrophthalide. The *picrate* melts at 158°, whilst the *platinochloride* crystallises in narrow, orange-yellow prisms and decomposes at about 120°, and the *aurichloride* crystallises well.
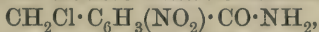
This compound and phthalimidine itself have the normal molecular weight, determined by the boiling point method. Hence it appears that phthalimidine has the constitution $C_6H_4\!<^{CO}_{CH_2}\!>\!NH$, whilst

pseudophthalimidine receives the formula assigned to it by Kiel. When orthocyanobenzylphthalimide is heated with hydrochloric acid at 190—200°, a small amount of phthalimidine is formed. In former experiments, this was isolated as nitrosophthalimidine, the formation of which was, however, ascribed to the action of the nitrous acid on the orthocyanobenzylamine which is also present in the product. Renewed experiments have, however, shown that orthocyanobenzylamine is not attacked by nitrous acid, but that it is converted into phthalimidine by the continued action of acids. This formation of phthalimidine affords further evidence in favour of the formula ascribed to it above. Orthocyanobenzylamine is best obtained by heating orthocyanobenzylphthalimide with alcoholic potash. The *hydrochloride* decomposes at about 207°, whilst the *picrate* melts and decomposes at about 219°.

Alcoholic potash cannot be employed for the preparation of other amines from their phthalimide compounds; benzylphthalimide, for example, when treated in this way, does not yield the amine, but is converted into *benzylphthalaminic acid*, $C_7H_7 \cdot NH \cdot CO \cdot C_6H_4 \cdot COOH$, which crystallises in needles and melts and decomposes at 154°, benzylphthalimide being again produced.   A. H.

Diazomethane and Nitroso-acidamides. By HANS VON PECH-MANN (*Ber.*, 1898, **31**, 2640—2646).—When nitrosomethylurethane is decomposed by alcoholic potash, only half the theoretical yield of diazomethane is obtained, and this is due to the fact that the remainder of the urethane is decomposed by the potash in the following ways. 1, Formation of nitrous acid and urethane, $NO \cdot NMe \cdot COOEt + H_2O = HNO_2 + NHMe \cdot COOEt$; 2, formation of carbonic acid, nitrous acid, and methylamine, $NO \cdot NMe \cdot COOEt + 2H_2O = OH \cdot COOEt + HNO_2 + NH_2Me$. Nitrosoethylurethane, nitrosobenzylurethane, and nitrosobenzoylbenzylamine are decomposed in a similar manner, whilst it has been found that benzylamine acts as an alkali in the same way as the potash. *Nitrosoethylurethane*, prepared in the same way as the methyl derivative, is an oil which boils at 90° under a pressure of 42 mm. and has a sp. gr. = 1·0735 at 15°/15°. When treated with alcoholic potash, 20 per cent. of the theoretical amount of *diazoethane* is produced; this is very similar to diazomethane, but its solution in ether is of a darker colour. When nitrosoethylurethane is treated with benzylamine, nitrogen is evolved and benzyl-urethane produced, the diazoethane, which is, no doubt, the first product, being immediately decomposed. *Benzylurethane* crystallises in colourless plates melting at 44°, and is converted by nitrous acid into *nitrosobenzylurethane*, which is a reddish-yellow oil, and cannot be distilled; when this is treated with alcoholic potash, it yields stilbene and benzylic methylic ether. *Nitrosobenzobenzylamide* crystallises in pinkish prisms, melts at 46—47°, and gradually decomposes when kept, yielding nitrogen and benzylic benzoate. When heated with alcohol, it decomposes in all the ways already described in the case of nitrosomethylurethane: (1) into benzoic acid and phenyl-diazomethane, which appears in the product partly as benzylic ethylic ether, and partly as benzylic benzoate; (2) into nitrous acid and

benzoylbenzylamine; and (3) into benzoic acid, nitrous acid, and benzylamine.

Attempts to bring about the direct elimination of nitrogen from diazomethane by heating it, and by the use of powdered copper, platinum black, &c., proved unsuccessful.   A. H.

New Representatives of Primary Disazo-dyes of the Benzene Series. By CARL BÜLOW and HANS WOLFS (*Ber.*, 1898, **31**, 2775—2783, Compare Abstr., 1898, i, 308).—The following additional colouring matters have been prepared; they have the general formula $NMe_2 \cdot C_6H_2(OH)(N_2R) \cdot N_2R'$ [$NMe_2 : OH : N_2R : N_2R' = 1:3:4:6$], and the groups tabulated under 4 and 6 are the groups R and R' respectively; the method of preparation is that already indicated.

4.	6.	Colour.	Melting point.
Ph	$1\text{-}C_{10}H_7$	Dark red	178°
$1\text{-}C_{10}H_7$		Violet-red	176
$1\text{-}C_{10}H_7$	Ph	Dark brown	180—181
Ph	$2\text{-}C_{10}H_7$	Claret-red	176
$2\text{-}C_{10}H_7$		Brown	196
$2\text{-}C_{10}H_7$	Ph	Brown	154
$2\text{-}C_6H_4Me$	$1\text{-}C_{10}H_7$	Black	185—186
$1\text{-}C_{10}H_7$	$2\text{-}C_6H_4Me$	Dark green	132
$2\text{-}C_6H_4Me$	$2\text{-}C_{10}H_7$	Dark brown	182
$2\text{-}C_{10}H_7$	$2\text{-}C_6H_4Me$	Dark green	187
$4\text{-}C_6H_4Me$	$1\text{-}C_{10}H_7$	Green	182
$1\text{-}C_{10}H_7$	$4\text{-}C_6H_4Me$	Dark brown	154—155
$4\text{-}C_6H_4Me$	$2\text{-}C_{10}H_7$	Red	153
$2\text{-}C_{10}H_7$	$4\text{-}C_6H_4Me$	Dark green	180
$2:4\text{-}C_6H_3Me_2$	$1\text{-}C_{10}H_7$	Dark red	147—148
$1\text{-}C_{10}H_7$	$2:4\text{-}C_6H_3Me_2$	Dark red	141
$2:4\text{-}C_6H_3Me_2$	$2\text{-}C_{10}H_7$	Red	175
$2\text{-}C_{10}H_7$	$2:4\text{-}C_6H_3Me_2$	Dark green	171—172

C. F. B.

Ketochlorides and Orthodiketones of Phenylazimidobenzene and Phenyl-ψ-azimidobenzene. By THEODOR ZINCKE and E. PETERMANN (*J. pr. Chem.*, 1898, [ii], **58**, 234—244. Compare Abstr., 1898, i, 537).—The paper contains a preliminary account (without experimental details) of experiments with phenylazimidobenzene and phenyl-ψ-azimidobenzene, carried out on similar lines to those already described with azimidobenzene (*loc. cit.*). Like the latter substance, they can be converted into ketochlorides and orthodiketones, possessing a strong analogy to those derived from azimidobenzene. The analogy is not complete, however, for the presence of the phenyl group, and the difference in constitution of the nitrogen ring, exert an influence on the results. For example, the phenyl group of the azimido-derivative does not react with chlorine, whereas substitution takes place in the phenyl group of the ψ-derivative.

A. W. C.

Hydrazides of Meta- and Para-bromobenzoic Acid. By THEODOR CURTIUS and EDUARD PORTNER (*J. pr. Chem.*, 1898, [ii], **58**, 190—205. Compare preceding abstract).—*Metabromobenzhydrazide*, $C_6H_4Br\cdot CO\cdot NH\cdot NH_2$, prepared from hydrazine hydrate and ethylic metabromobenzoate according to directions already given (*J. pr. Chem.*, [ii], **50**, 295), forms long, glistening, silken needles, melts at 151°, is soluble in alcohol, but almost insoluble in ether, chloroform, and benzene, and reduces Fehling's solution and ammoniacal silver nitrate in the cold. The *hydrochloride* forms small leaflets melting and giving off gas at 248°; the *sodium* salt, small plates; and the *acetyl* derivative colourless, silken prisms melting at 169°.

Benzylidenemetabromobenzhydrazine, $CHPh\dot{:}N\cdot NH\cdot CO\cdot C_6H_4Br$, prepared by the action of benzaldehyde on the hydrazide, crystallises from alcohol in beautiful, long, colourless needles melting at 105°; boiling dilute mineral acids decompose it into its components. The corresponding *orthohydroxybenzylidene* compound forms tufts of colourless needles melting at 192°, and the *acetone* [β-propylidene] derivative, small needles melting at 88·5°. *Dimetabromobenzhydrazide*, $(NH\cdot CO\cdot C_6H_4Br)_2$, obtained by the action of iodine on the bromobenzhydrazide, crystallises from glacial acetic acid in small, glistening needles melting at 265°. When boiled with dilute mineral acids, it is converted into bromobenzoic acid and a hydrazine salt.

Metabromobenzazide, $C_6H_4Br\cdot CO\cdot N_3$, obtained by the action of nitrous acid on bromobenzhydrazide, is a colourless oil with an unbearable odour producing tears, and explodes violently when heated in a test tube.

Metadibromodiphenylcarbamide, $CO(NH\cdot C_6H_4Br)_2$, prepared from the azide by boiling with water, forms long, colourless, silken prisms melting at 262°. It is volatile without decomposition, sublimes in small needles, and, when boiled with acids, is decomposed into metabromaniline and carbonic anhydride.

Ethylic metabromophenylcarbamate, $C_6H_4Br\cdot NH\cdot COOEt$, obtained by the action of absolute alcohol on metabromobenzazide, is a thick, colourless oil boiling at 193—194° under a pressure of 17 mm., and is decomposed into its components by concentrated acids. The corresponding *methylic* salt is a colourless oil boiling at 165—167° under a pressure of 75 mm.

The following corresponding *para*-compounds are also described.

Bromobenzhydrazide, long, colourless prisms melting at 164°; its *hydrochloride*, small, glistening needles melting at 262°; *acetone-*[β-propylidene]*bromobenzhydrazide*, long needles melting at 194·5°; *benzylidenebromobenzhydrazide*, colourless, silken prisms melting at 235°; *bromobenzazide*, colourless plates melting at 46°; *ethylic bromophenylcarbamate*, long, white needles melting at 81°; the corresponding *methylic* salt melts at 81°; *dibromodiphenylcarbamide*, clusters of nacreous needles melting at 274°; and *bromophenylbromobenzoylsemicarbazide*, $C_6H_4Br\cdot NH\cdot CO\cdot N_2H_2\cdot C_6H_4Br$, microscopic plates melting at 248°.

When parabromobenzazide is dissolved in carbon tetrachloride, and bromine added, a colourless, crystalline substance, probably dibromocarbanil, is obtained,   A. W. C.

Phenylsemicarbazide. By THEODOR CURTIUS and ADOLF BURKHARDT (*J. pr. Chem.*, 1898, [ii], **58**, 205—233. Compare Abstr., 1896, i, 647).—In continuance of the researches of Curtius and Hofmann (*loc. cit.*), it is now shown that phenylcarbamazide does not undergo rearrangement, as do ordinary acid azides of the type $RCON_3$. When heated with water in sealed tubes, it is completely converted into carbonic anhydride, diphenylcarbamide and hydrazoic acid; alcohol decomposes it into hydrazoic acid and phenylurethane; aniline produces the carbanilide, and bromine gives *parabromophenylcarbamazide*, $C_6H_4Br \cdot NH \cdot CO \cdot N_3$, separating from alcohol in rhombic crystals melting at 126°, which are acted on by water, with production of paradibromocarbanilide.

The solid, microcrystalline product formed on adding sodium nitrite to an aqueous solution of oxalhydrazide hydrochloride is not a product of the rearrangement of the oxazide, but the dihydrazide of oxalic acid, produced by the oxidation of the hydrazide.

Phenylsemicarbazide may be obtained by the action of hydrazine hydrate on (*a*) the phenylurethanes, $NHPh \cdot COOR + N_2H_5OH = NHPh \cdot CO \cdot NH \cdot NH_2 + ROH + H_2O$; (*b*) on mono- or di-phenylcarbamide, $CO(NHPh)_2 + N_2H_5 \cdot OH = NHPh \cdot CO \cdot NH \cdot NH_2 + NH_2Ph + H_2O$; (*c*) on phenylcarbimide. The best yields are obtained from diphenylcarbamide, all the other reactions being more or less complicated, and the isolation of the base difficult.

Phenylsemicarbazide *hydrochloride* forms colourless, transparent prisms melting at 215°; the *sodium* compound crystallises in yellowish needles, and the *acetyl* derivative in colourless needles melting at 169°.

Ethylic phenylsemicarbazideacetoacetate,

$$NHPh \cdot CO \cdot NH \cdot N:CMe \cdot CH_2 \cdot COOEt,$$
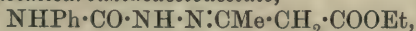
formed by the interaction of ethylic acetoacetate and the semicarbazide, crystallises from alcohol in small, colourless needles melting at 151°.

Hydrazidicarbonanilide, $NHPh \cdot CO \cdot NH \cdot NH \cdot CO \cdot NHPh$, obtained by the action of iodine or of heat alone on phenylsemicarbazide, crystallises from glacial acetic acid in long, colourless prisms melting at 245°, without decomposition, is with difficulty soluble in the ordinary organic solvents, and possesses basic properties. When heated with hydrochloric acid in sealed tubes, at 180—200°, it is completely converted into carbonic anhydride, aniline, and hydrazine hydrochloride. Bromine acts on it in glacial acetic acid solution, forming a *tetrabromo*-compound, $C_{14}H_{12}N_4Br_4$, crystallising in needles and melting at 215—218°.

Azo-dicarbonanilide, $N_2(CO \cdot NHPh)_2$, produced by the action of nitric acid on hydrazidicarbonanilide, crystallises from acetone in bunches of dark red needles melting at 182—183°. On rubbing, the substance becomes strongly electric, and is reconverted into hydrazidicarbonanilide by boiling with acids, alkalis, or tin and hydrochloric acid.

Phenylcarbaminazide, $NHPh \cdot CO \cdot N_3$, prepared by the action of

sodium nitrite on an aqueous solution of phenylsemicarbazide hydro-
chloride, crystallises in colourless leaflets melting at 103—104°.

<div align="right">A. W. C.</div>

Catecholglyoxal. By CHARLES MOUREU (*Compt. rend.*, 1898,
127, 324—326).—The compound, $C_8H_8O_4$, obtained by J. Hesse by
boiling with dilute sulphuric acid the product, $C_6H_4:O_2:CH\cdot CH(OEt)_2$,
prepared by the action of dichloracetal on disodiumcatechol, is
identical with the hydroxyphenoxyacetic acid obtained by the author
under similar conditions from dicatecholacetylenic ether. It is clear
that, although the aldehyde catecholglyoxal has not been isolated, it
must be the first product of the hydration of the compound

$$C_6H_4:O_2:CH\cdot CH(OEt)_2,$$
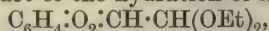
and hence may be assumed to be an intermediate product in the
hydration of catechol acetylenic ether, since the final product is the
same in both cases (compare this vol., i, 125).   C. H. B.

**Benzoyl Derivatives of Acetonitrile and Paratoluoylaceto-
nitrile.** By O. SEIDEL (*J. pr. Chem.*, 1898, [ii], 58, 129—159).—
Benzoylacetonitrile (cyanacetophenone) is best obtained by the
action of concentrated hydrochloric acid on benzacetodinitrile.
Obregia (Abstr., 1892, ii, 324) obtained from it, by the action
of phenylhydrazine, a yellow, crystalline substance melting at
134—135°, whereas Burns (Abstr., 1893, i, 314), by the action of phenyl-
hydrazine on benzacetodinitrile, obtained yellow needles melting
at 121°, although the reaction should give the same substance as that
obtained by Obregia. The author now shows that the two substances
are identical, and must be regarded as the *phenylhydrazone* of cyan-
acetophenone melting at 146—147°, the difference in the observed
melting points being accounted for by the fact that, on warming, or on
exposure to air, or by repeated crystallisation from dilute alcohol or
chloroform, it is partially converted into an isomeride, 1 : 3-*diphenyl-
5-imidopyrazoline*, $C_{15}H_{13}N_3$, crystallising in white, rhombic plates and
melting at 129·5°; this cannot be reconverted into the phenylhydr-
azone, than which it is much more stable, and possesses basic
properties.

The *hydrochloride* is not stable in air, and the *platinochloride* crystal-
lises in large, prismatic needles melting and decomposing at 191°.
Both isomerides, when treated with acetic anhydride, give the same
monacetyl derivative, crystallising from benzene in beautiful, white
needles melting at 149°.

When the phenylhydrazone is treated with nitrous acid in ether,
benzene, alcohol, or chloroform solution, nothing but tarry products are
produced, but when dissolved in acetic acid, whereby it is converted
into its isomeride, two substances are formed which can be separated by
the difference in their solubilities in acetic acid or benzene; the one is the
true *nitroso*-derivative of diphenylimidopyrazoline, $C_{15}H_{12}N_4O$, crystal-
lising from benzene in dark red, glistening prisms melting at 207°,
which, when heated with concentrated hydrochloric acid, is converted
into 4-isonitroso-1 : 3-diphenylpyrazolone (compare Knorr and Klotz,

(Abstr., 1887, 1121), and the other, of the composition $C_{30}H_{23}N_7$, crystallises from glacial acetic acid in canary-yellow needles, melting at 217°. It is not acted on by concentrated sulphuric acid or hydrochloric acid when heated with it in sealed tubes at 160°, and is probably formed by the condensation of 1 molecule of the red substance with 1 molecule of the imidopyrazoline.

Phenylhydrazine reacts with paratoluacetodinitrile, forming a *phenylhydrazone* crystallising in yellow needles and melting at 153°. When heated, or dissolved in acetic acid, it is converted into the isomeric 1-phenyl-3-paratolyl-5-imidopyrazoline, from which, by the action of nitrous acid a *red* substance, $C_{16}H_{14}N_4O$, melting at 232°, and a *yellow* substance, $C_{32}H_{37}N_7$, melting at 212°, are produced.

Burns (*loc. cit.*) and Obregia (*loc. cit.*) have stated that cyanacetophenoneoxime is only stable in the form of its isomeride phenylisoxazoloneimide, whereas Probst believes the oxime of paratolylacetodinitrile to be a true oxime. The author cannot substantiate Probst's conclusions, and regards the substance as γ-paratolylimidoisoxazoline.

Cyanacetophenone diphenylhydrazone, $C_{21}H_{17}N_3$, obtained by the action of diphenylhydrazine on an alcoholic solution of cyanacetophenone, crystallises from dilute alcohol in yellow prisms melting at 148°; it cannot be converted into an isomeride either by the action of heat or by dissolving it in glacial acetic acid.

3-Phenyl-5-imidopyrazoline, $C_9H_9N_3$, produced by the action of hydrazine sulphate on cyanacetophenone, forms white crystals melting at 125°. The *hydrochloride* crystallises in small needles, and the *platinochloride* forms large, yellow prisms melting and decomposing at 225°.

1 : 3 : 5-Triphenyl-4-cyanopyrazole, $C_{22}H_{15}N_3$, obtained by the interaction of dibenzoylacetonitrile and phenylhydrazine hydrochloride, crystallises from alcohol in white needles melting at 189°, is insoluble in potassium hydroxide, is not attacked by hydrochloric acid when heated with it in sealed tubes at 160°, or by sulphuric acid, in which it is soluble, and does not form a platinochloride; when hydrolysed, it is converted into *1 : 3 : 5-triphenyl-4-pyrazolecarboxylic acid,* which crystallises in white needles melting at 238°, and when heated alone, is changed into 1 : 3 : 5-pyrazole, with loss of carbonic anhydride.

When the silver salt of dibenzoylacetonitrile is treated with methylic iodide, the *methylic* salt is obtained in small, yellow needles melting at 117—118°; it is neutral, and is readily decomposed by water into dibenzoylacetonitrile and methylic alcohol.

Tribenzoylacetonitrile, $CN \cdot CBz_3$, or $CN \cdot CBz \colon CPh \cdot OBz$, obtained from the above silver salt by the action of benzoic chloride, forms compact, white crystals melting at 138°. Alkalis decompose it at once into dibenzoylacetonitrile and benzoic acid; aniline gives the corresponding *anilide* crystallising from alcohol in silken needles melting at 165°, and phenylhydrazine produces 1 : 3 : 5-triphenyl-4-cyanopyrazole.

During the original reaction (benzoic chloride and acetonitrile), a *substance,* $C_{17}H_{12}N_2O$, is also produced, crystallising in golden needles melting at 204°; it could not be obtained in quantity sufficient for complete investigation.   A. W. C.

Condensations with Phenylacetone [Benzyl Methyl Ketone]. II. By GUIDO GOLDSCHMIEDT and GUSTAV KNÖPFER (*Monatsh.*, 1898, **19**, 406—426. Compare Abstr., 1898, i, 31).—The ketone, $C_{16}H_{15}ClO$, obtained by the action of hydrochloric acid on a mixture of benzyl methyl ketone and benzaldehyde, may be made to yield stilbene by distillation with lime. It dissolves gradually in cold, strong sulphuric acid, giving a colourless solution, which becomes yellow and finally brown when warmed.

When heated with an alcoholic solution of hydroxylamine hydrochloride, chlorobenzylphenylacetone, as the author terms the above ketone, yields an *oxime*, $C_{16}H_{15}NO$, which crystallises in beautiful, colourless, silky needles, melts at 153°, and is insoluble in alkalis or acids; when boiled with acetic anhydride, it affords a *substance*, possibly an acetyl derivative, which crystallises from alcohol in beautiful, white needles, and melts at 92°.

When chlorobenzylphenylacetone is warmed, in alcoholic solution, with an equal weight of potassium cyanide, a *compound*, $C_{17}H_{15}NO$, is produced which crystallises from alcohol in needles and melts at 193°; it sublimes without decomposing, and dissolves in strong sulphuric acid, giving a yellow solution which, when warmed, exhibits a feeble violet fluorescence. It was not possible to obtain the corresponding acid by hydrolysis.

The ketone, $C_{16}H_{14}O$ (m. p. = 53°, *loc. cit.*), yields a thick oil on distillation with lime, but stilbene could not be detected in it. The ketone dissolves in sulphuric acid, giving an emerald green solution, which assumes a bluish-violet fluorescence when warmed. It is at once destroyed by permanganate solution, but is not appreciably affected by potassium hydroxide, or dilute alcoholic hydrochloric acid. It does not yield a crystallisable additive product with bromine.

The ketone, $C_{16}H_{14}O$ (m. p. = 71°), comports itself towards permanganate and on distillation exactly like its isomeride. Its solution in sulphuric acid is lemon-yellow, and, when warmed, becomes red, exhibiting a strong green fluorescence. It evolves the odour of benzaldehyde when warmed with alcoholic hydrochloric acid, and the solution on cooling, especially after dilution, deposits oily drops and crystals of the unaltered substance. The *dibromide*, $C_{16}H_{14}OBr_2$, made by adding bromine to a solution of the ketone in chloroform, crystallises in beautiful, silky needles, melts at 93°, and dissolves very readily in ether and benzene, but only sparingly in alcohol and light petroleum.

Triphenyltetrahydro-γ-pyrone, when warmed with alcoholic hydrochloric acid, is decomposed into benzaldehyde and the ketone melting at 71°; the inverse change is effected by shaking a mixture of benzaldehyde and the unsaturated ketone with aqueous potash during 48 hours; the saturated ketone does not afford the pyrone derivative under these conditions; under certain circumstances, the substance melting at 175° is also formed by this process of condensation (*loc. cit.*). The analysis and molecular weight of the latter compound points to the formula $C_{41}H_{38}O_3$, hence its formation from benzyl methyl ketone and benzaldehyde is probably effected in similar manner to that of dibenzylidenetriacetophenone, by the condensation of acetophenone and benzaldehyde; its constitution is probably, therefore,

$COMe \cdot CPh(CHPh \cdot CHPh \cdot COMe)_2$. Benzylidenetriphenylacetone dissolves in strong sulphuric acid, and forms a lemon-yellow solution, which darkens spontaneously and becomes ruby-red when warmed.

When hydrogen chloride is passed into an imperfectly cooled mixture of benzyl methyl ketone and benzaldehyde, a substance, $C_{25}H_{22}O$, is sometimes obtained; this forms yellowish crystals, melts at 140°, and may be distilled without decomposing. It is probably produced by the condensation of an intermediate 1 : 5-diketone in the usual manner, being, therefore, 1-*methyl*-2 : 3 : 4-*triphenylcyclo*-Δ^6-*hexenone*-5, $CMe{<}^{CHPh \cdot CHPh}_{CH \underline{\quad\quad} CO}{>}CHPh$. It gives an *oxime*, $C_{25}H_{21}NO$, which forms aggregates of crystals, melts at 204°, and dissolves sparingly in alcohol, but readily in other media.

Dibenzyl ketone and benzaldehyde condense in presence of dry hydrogen chloride, forming a *substance* which has the composition $C_{22}H_{19}ClO$, and is, therefore, the hydrogen chloride additive product of benzylidene dibenzyl ketone; it melts at 143°, and, on distillation, yields phenylacetic chloride and stilbene.

Of the above isomeric ketones, $C_{16}H_{14}O$, that melting at 53° is saturated and produced by a ready elimination of hydrogen chloride from the substance $C_{16}H_{15}ClO$, and is, therefore, in all probability a cyclic compound, 1-phenyltetrahydro-β-naphthenone,

$$C_6H_4{<}^{CHPh \cdot CH_2}_{CH_2 \underline{\quad} CO},$$
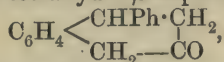
whilst the isomeric unsaturated ketone (m. p. = 71°) probably has the constitution $CHPh{:}CPh \cdot COMe$.

The hydrocarbon melting at 120°, which was obtained from benzaldehyde and benzyl methyl ketone by the use of sulphuric acid (*loc. cit.*), turns out to be stilbene (compare Miller and Rohde, Abstr., 1890, 978). A. L.

Solubilities of the Nitrobenzoic Acids. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1898, **17**, 247—258).—The following table gives the solubilities of ortho-, meta- and para-nitrobenzoic acids in water, chloroform, and absolute alcohol at temperatures of 15°, 25°, and 35°; the numbers represent grams of acid dissolved in 100 grams of the solvent, except in the case of alcohol, when they represent gram-molecules per litre.

Nitrobenzoic acid.	Water at			Chloroform at			Absolute alcohol at 15°.
	15°.	25°.	35°.	15°	25°.	35°.	
Ortho	0·625	0·744	1·141	1·06	1·13	1·59	2·25
Meta	0·238	0·305	0·477	3·45	4·70	6·31	2·83
Para	0·0213	0·0235	0·0419	0·088	0·114	0·156	0·118

The solubility in water of a mixture of the para-acid with either the ortho- or meta-acid is approximately equal to that calculated

from Nernst's theory of the diminution in solubility of one substance in presence of another having an ion in common with it. An increase of solubility of the three acids occurs, however, when they are all present simultaneously in solution; and the same is true of a mixture of the ortho- and meta-acids. To explain this anomaly, combination is assumed to take place between the substances present together (compare Le Blanc and Noyes, Abstr., 1891, 388); this would elucidate the difficulty experienced in separating ortho- and meta-nitrobenzoic acids by crystallisation from water.   W. A. D.

Piperonal Derivatives. By S. BAUDE and ALBERT REYCHLER (*Bull. Soc. Chim.*, 1897, [iii], 17, 616—618).—*Ethylic methylenedioxycinnamate*, $CH_2\!<^O_O\!>C_6H_3\cdot CH\!:\!CH\cdot COOEt$, obtained by the action of metallic sodium on a mixture of piperonal and ethylic acetate, crystallises in needles melting at 65—68°, is soluble in alcohol and ether, and distils, with slight decomposition, at about 317°. Its *dibromide* forms colourless plates melting at 84°, and is readily soluble in ether or alcohol, but insoluble in light petroleum.

Methylenedioxyphenylpropiolic acid, $CH_2\!<^O_O\!>C_6H_3\cdot C\!:\!C\cdot COOH$, obtained when the dibromide is repeatedly boiled with alcoholic potash, crystallises from dilute alcohol in pale yellow needles, turns brown at 145°, and melts and decomposes at 166°.

Methylenedioxyphenylacetylene, obtained by heating the above acid with three to four times its weight of dry aniline at 150—160°, is a yellow oil.   J. J. S.

Condensation of Phthalaldehydic Acid with Acetone and Acetophenone. By ARTHUR HAMBURGER (*Monatsh.*, 1898, 19, 427—455. Compare Goldschmiedt, Abstr., 1892, 179, and Hemmelmayr, Abstr., 1893, i, 181, and 1894, i, 151).—Phthaldehydic acid and acetone condense readily at 40—60° in presence of dilute soda; the liquid, after remaining for 24—48 hours, is acidified with hydrochloric acid, when the mixture acquires a milky appearance, and a gelatinous precipitate slowly forms. This is separated by filtration, washed, and dissolved in alcohol, from which, on cooling, *diphthalidedimethyl ketone*, $(CO\!<^{C_6H_4}_{\;O}\!>CH\cdot CH_2)_2CO$, crystallises in the form of white, felted needles which melt at 156—157°. On evaporating the filtrate from the above precipitate, or extracting it with ether, it yields a much larger quantity of a second substance, *phthalidedimethyl ketone*, $CO\!<^{C_6H_4}_{\;O}\!>CH\cdot CH_2\cdot COMe$, which crystallises from water in quadratic plates of considerable size and melts at 67—68°, dissolves readily in water, alcohol, ethylic acetate, and benzene, and more sparingly in chloroform and light petroleum. Both compounds dissolve slowly in cold, but readily in hot, potash, giving intensely yellow colorations; with bromine, they give substitution, not additive, compounds.

Diphthalidedimethyl ketoxime, $C_{19}H_{15}O_5N$, is nearly insoluble in water,

acetic acid, ethylic acetate, and benzene, and only very sparingly in alcohol, methylic alcohol, ether, acetone, and chloroform, but dissolves readily in cold potash, and is reprecipitated by acids; it is indistinctly crystalline, sinters at 181°, and melts at 197—203°.

When hydroxylamine acts on phthalidedimethyl ketone, two isomeric *oximes*, $C_{11}H_{11}NO_3$, are formed; one of these, obtained by acidifying the product with hydrochloric acid, crystallises from dilute alcohol in yellowish forms and melts at 127—128°; it dissolves very readily in methylic or ethylic alcohol or ether, less readily in water, sparingly in benzene and chloroform, and is more easily soluble in alkali than in water. The second oxime is formed by dissolving the first in boiling water, from which it separates in white, felted leaflets, or by heating it for some at 100°; it melts at 59—61°, and dissolves readily in the usual media and in alkalis. Both oximes, when treated with the "Beckmann mixture," give an oil and an *acetyl* compound, $C_{13}H_{13}NO_4$; this forms slender needles, and on warming with fuming hydrochloric acid gives phthalidedimethyl ketone.

Phthalidedimethyl ketone reacts with phenylhydrazine and with bromine, hydrogen bromide being evolved in the latter instance; in neither case, however, is a crystalline compound produced.

Phthalaldehydic acid and acetophenone interact in presence of soda at 40°; the product, *phenyl phthalidemethyl ketone*, $\begin{smallmatrix}C_6H_4\\COO\end{smallmatrix}{>}CH{\cdot}CH_2{\cdot}COPh$,

crystallises from alcohol in long, white, felted needles, and melts at 141—142°. It dissolves instantly in warm alkalis, with a yellow coloration, and is sparingly soluble in water and ether, but dissolves somewhat readily in alcohol.

Phenyl phthalidemethyl ketoxime, $C_{16}H_{13}NO_3$, forms white needles, sinters at 177°, and melts at 181—182°; a second substance is obtained simultaneously which is insoluble in soda, and decomposes, evolving gas, at 180° and melts at 215°. The former is somewhat readily soluble in alcohol, ether, and hot benzene, and is very unstable in presence of light, becoming yellow; potash quickly dissolves it, but it is deposited unaltered on adding an acid. When subjected to treatment with "Beckmann's mixture," it yields

3-carboxyphenyl-5-phenylisoxazoline, $CPh{<}\begin{smallmatrix}N{\cdot}O\\CH_2\end{smallmatrix}{>}CH{\cdot}C_6H_4{\cdot}COOH$.

Bromine acts on phenyl phthalidemethyl ketone, hydrogen bromide being evolved, but the product is not crystalline; it is not affected when shaken with benzylic chloride and aqueous soda.

When a mixture of phenylhydrazine and phenyl phthalidemethyl ketone is warmed on the water-bath, a *substance* of the composition $C_{22}H_{18}N_2O_2$, probably $CO{<}\begin{smallmatrix}C_6H_4\\N_2HPh\end{smallmatrix}{>}CH{\cdot}CH_2{\cdot}COPh$, is formed. This crystallises from alcohol in yellowish, glistening needles and melts at 118—123°; it is very readily soluble in chloroform and alcohol, somewhat less readily in benzene and acetic acid, sparingly in ether, and is nearly insoluble in water. When heated with strong sulphuric acid, it becomes dark-red, but quickly dissolves, forming a yellow solution which soon becomes green, especially on the addition of a drop of

solution of ferric chloride. It does not reduce Fehling's solution, and is not affected by hot alkalis or by concentrated hydrochloric acid.

An isomeric *compound*, $C_{22}H_{18}N_2O$, possibly

$$COOH \cdot C_6H_4 \cdot CH{<}^{CH_2 \cdot \ CPh}_{NPh \cdot N},$$
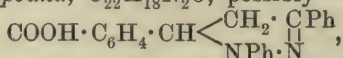
is produced when phenyl phthalidemethyl ketone and phenylhydrazine are heated together in sealed tubes at 170—190° for 5 hours. It crystallises from alcohol in rosettes of needles and melts between 170° and 200°, is sparingly soluble in benzene, but dissolves readily in alcohol, ether, glacial acetic acid, and nitrobenzene. Its solution in concentrated sulphuric acid is red, becoming dark blue on the addition of a drop of ferric chloride, owing to the formation of a sparingly soluble blue compound, and on adding potassium dichromate, a violet coloration is produced which changes successively to dark blue, red, and yellowish-brown; in the latter instance, subsequent dilution of the liquid causes the separation of a red precipitate; dilute nitric acid instantly turns the substance blue; it does not reduce Fehling's solution. It dissolves in sodium carbonate solution, producing a liquid which readily forms a lather, and when excess of soda is used, a *sodium* salt is formed, which crystallises in beautiful, transparent needles.

The first isomeride, when heated in a closed tube at 170°, suffers almost complete conversion into the second.

When phenyl phthalidemethyl ketone is heated at 170—190° in sealed tubes with phenylhydrazine (2 mols.), a third *substance*, $C_{28}H_{24}N_4O$, possibly $CO{<}^{-C_6H_4-}_{NH \cdot NPh}{>}CH \cdot CH_2 \cdot CPh{:}N \cdot NHPh$, is obtained, which is nearly insoluble in water, alcohol, ether, and light petroleum, but dissolves readily in hot amylic alcohol, ethylic acetate, and glacial acetic acid, sinters at 157°, and melts at 163—175°. Sulphuric acid dissolves it, forming a dark green solution in which a trace of ferric chloride, potassium dichromate, or sodium nitrite produces a red coloration. It is insoluble in boiling alkalis, and does not reduce Fehling's solution.　　　　　　　　　　　　　　A. L.
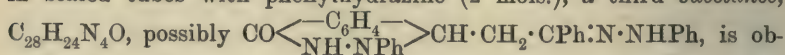
Behaviour of Phthalide on Distillation with Lime. By HANS KRCZMAŘ (*Monatsh.*, 1898, **19**, 456—460).—A mixture of phthalide and lime was cautiously heated at about 290° in a long glass tube, through which a slow stream of hydrogen was passed; the distillate contained a clear liquid and a crystalline solid. The liquid portion consisted for the most part of benzene and probably, in part, of toluene, as on oxidation with chromic acid the odour of benzoic acid made itself perceptible. The solid substance was anthracene, probably contaminated with diphenyl.　　　　　　　　　　　　　A. L.

Condensation of Malonic Acid with Aromatic Aldehydes by means of Ammonia and Amines. By EMIL KNOEVENAGEL [and in part FR. BAEBENROTH and O. WOLLWEBER] (*Ber.*, 1898, **31**, 2596—2619). —When malonic acid is warmed with substituted benzylidenebisalkylamines or benzylidenebisdialkylamines, interaction as a rule takes place readily, and acids of the acrylic or malonic series are produced. In the case of benzylidenebispiperidine and malonic acid, the action is represented by the equation $CHPh(C_5NH_{10})_2 + CH_2(COOH)_2 = CHPh{:}CH \cdot COOH + CO_2 + 2C_5H_{11}N.$

Many benzylidenealkylamines act in a similar manner, but by using benzylidine-α(or β)-naphthylamine and benzylidenemetanitraniline, no cinnamic acid was obtained.

Hydrobenzamide reacts with malonic acid in a fashion which is analogous to the behaviour of other substituted benzylideneamines; the equation is $N_2(CHPh)_3 + 3CH_2(COOH)_2 = 3CO_2 + 2NH_3 + 3CHPh:CH \cdot COOH$.

Salicylideneaniline and malonic acid yield coumarincarboxylic acid, aniline, and water. It is not necessary to isolate the salicylideneaniline, mere addition of aniline to a solution of malonic acid and salicylic acid, or of the aldehyde to aniline malonate, being all that is required. Similar results with analogous trios of substances have shown that, in general, the order of interaction exerts only a quantitative influence on the product obtained.

The intermediate product in these reactions, namely, the alkylidinemalonic acid, may be isolated if the temperature of the reaction be kept sufficiently low, the optimum point depending on the nature both of the base and of the aldehyde employed. With ammonia, the temperature at which carbonic anhydride is eliminated is lower than where aniline is the condensing agent, and, in consequence, a smaller yield of alkylidenemalonic acid is obtained.

It is to be noted that the requisite proportion of base varies with the nature both of the base itself and of the aldehyde used; it is found, moreover, that, with some bases, little or none of the desired products are obtainable. The necessary duration of the action is also found to vary; in some cases, a short time only is advisable, and in others the reverse holds true.

The paper concludes with a detailed description of the experiments on which the foregoing statements are based, and the following substances are described for the first time.

Anisylidenemalonic acid is obtained when anisaldehyde (1·3 grams) and normal ammonium malonate (1·4 grams) are covered with alcohol and the whole rapidly evaporated on the water-bath nearly to dryness, and is precipitated by means of sulphuric acid from its alkaline solution as a yellow, flocculent substance which melts and effervesces briskly at 185—189°; it yields paramethoxycinnamic acid when boiled with alcohol.

Piperonylidenemalonic acid is made by warming piperonal with malonic acid and alcoholic ammonia (2 mols.) or with normal ammonium malonate. It is thrown down from its solution in soda, on acidification, as a white, flocculent precipitate, which melts and effervesces at 190—195°.

When a mixture of furfuraldehyde and malonic acid is cooled and treated with aniline, the whole soon solidifies and, on subsequently adding hydrochloric acid, crystals of a nitrogenous substance are deposited; this is sparingly soluble in water and dissolves in alcohol, forming a red solution which deposits violet crystals having a metallic lustre. It is completely destroyed by warm soda, and when warmed with sodium carbonate solution the colour is destroyed, but is restored on adding an acid.   A. L.

Condensations of Acid Derivatives of Ethylic Malonate with Ethylic Benzylideneacetoacetate. By EMIL KNOEVENAGEL and W. FABER (*Ber.*, 1898, **31**, 2768—2772).—When ethylic benzylideneacetoacetate (Abstr., 1896, i, 232) and either ethylic isobutyrylmalonate (see below) or ethylic benzoylmalonate (Claisen, *Annalen*, 1896, **291**, 72), are heated with a little alcohol until a homogeneous mixture has been formed, alcoholic potassium ethoxide then added, and the whole allowed to remain for several days, the product in both cases is diethylic 5-phenyl-1 : 3-diketocyclohexane-4 : 6-dicarboxylate (Abstr., 1894, i, 576), the isobutyryl or benzoyl group being removed.

$$CO{<}^{CH_3}_{C(COOEt):CHPh} + COOEt \cdot CHBz \cdot COOEt \longrightarrow$$

$$CO{<}^{CH_2 \text{------} CO}_{CH(COOEt) \cdot CHPh}{>}CH \cdot COOEt.$$
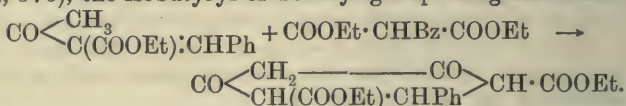
Ethylic isobutyrylmalonate, $CHMe_2 \cdot CO \cdot CH(COOEt)_2$, prepared from isobutyric chloride and ethylic sodiomalonate, boils at 133—134° under 14 mm., and at 126—127° under 10 mm. pressure.   C. F. B.

Condensing Action of Diethylamine. By EMIL KNOEVENAGEL and W. FABER (*Ber.*, 1898, **31**, 2773—2775).—When ethylic benzylideneacetoacetate, $CHPh{:}CAc \cdot COOEt$ (Abstr., 1896, i, 232), dissolved in a little alcohol, ethylic cuminylideneacetoacetate (Abstr., 1898, i, 404), or benzylideneacetylacetone (Abstr., 1895, i, 50), is mixed with a little diethylamine and allowed to remain, the product is ethylic benzylidenediacetoacetate, $CHPh(CHAc \cdot COOEt)_2$ (Abstr., 1896, i, 210; Hantzsch, Abstr., 1886, 77), ethylic cuminylidenediacetoacetate or benzylidenediacetylacetone respectively. In the first case, a similar condensation took place, even when ethylic isobutyrylmalonate was present; no condensation with the latter substance occurred.

C. F. B.

Orthaldehydophenoxy-acids. By HERMANN CAJAR (*Ber*, 1898, **31**, 2803—2811).—*Sodiosalicylaldehyde*, $CHO \cdot C_6H_4 \cdot ONa$, was prepared by treating salicylaldehyde with sodium ethoxide in the presence of a large quantity of alcohol; it is lemon-yellow. When it is suspended in benzene and treated with ethylic chloroformate, and the product distilled under 90 mm. pressure, an oil comes over at 197°, which is presumably *ethylic orthaldehydophenylic carbonate*,

$$CHO \cdot C_6H_4 \cdot O \cdot COOEt.$$
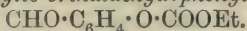
Alcoholic soda appears to hydrolyse this to the sodium salt, but the latter is at once decomposed by water, with formation of salicylaldehyde; the ethylic salt forms, however, a yellowish *phenylhydrazone* melting at 101—102°, and with aqueous semicarbazide hydrochloride, a yellow *product* melting at 111°, which apparently has the composition $COOEt \cdot O \cdot C_6H_4 \cdot CH{:}N \cdot NH \cdot CO \cdot N{:}CH \cdot C_6H_4 \cdot O \cdot COOEt$; with aqueous hydrazine hydrate, it yields *salicylaldehyde hydrazone*, $NH_2 \cdot N{:}CH \cdot C_6H_4 \cdot OH$, melting at 96° (this can also be obtained by adding a solution of hydrazine hydrate in dilute alcohol to an alcoholic solution of salicylaldehyde; when treated with acids, it yields Curtius and Jay's hydroxybenzalazine [Abstr., 1889, 393]); with salicylalde-

hyde hydrazone, the ethylic salt yields a *compound*,

OH·C$_6$H$_4$·CH:N·N:CH·C$_6$H$_4$·O·COOEt,
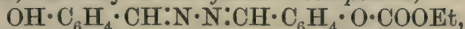
which melts at 114—115°, and forms hydroxybenzalazine when treated with acids (salicylaldehyde hydrazone also forms a *compound*, melting at 113—114°, with ethylic acetoacetate) ; with hydrazine sulphate in aqueous solution, it forms the *compound* N$_2$(:CH·C$_6$H$_4$·O·COOEt)$_2$, which is bright yellow and melts at 109—110°. With hydroxylamine, the ethylic salt does not react ; by warming salicylaldoxime with ethylic chloroformate in concentrated alcoholic solution, a *compound* melting at 69·5° is obtained, but this, probably, has the constitution COOEt·O·N:CH·C$_6$H$_4$·OH, for salicylaldehyde itself does not react in an analogous fashion. With ethylic malonate, after 3 hours heating on the water-bath, the ethylic salt forms coumarincarboxylic acid,

$$C_6H_4 \begin{array}{c} O\!-\!CO \\ \diagdown \quad | \\ CH\!:\!C\!\cdot\!COOH \end{array}$$ (Stuart, Trans., 1886, **49**, 366).
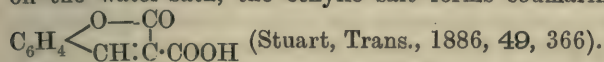
Orthaldehydophenoxyacetic acid (Rössing, Abstr., 1885, 388) was prepared by heating salicylaldehyde (1 mol.) with monochloracetic acid (1 mol.) and aqueous caustic soda (2 mols.) of sp. gr. = 1·2 ; when boiled with 3 per cent. methyl alcoholic hydrochloric acid, it yields the *methylic* salt, CHO·C$_6$H$_4$·O·CH$_2$·COOMe, which melts at 55—56°, and forms a yellow *hydrazone*, N$_2$(:CH·C$_6$H$_4$·O·CH$_2$·COOMe)$_2$, melting at 159—160° (the allied opianic acid yields a *pseudo*-salt ; compare Wegscheider, Abstr., 1892, 1208). With hydrazine hydrate, the acid gives a yellow *hydrazone*, N$_2$(:CH·C$_6$H$_4$·O·CH$_2$·COOH)$_2$, which melts and decomposes at 222° (and not a phthalazone ; compare Abstr., 1893, 371). When heated with hydroxylamine hydrochloride in 80 per cent. alcoholic solution, it yields the *ethylic* salt of orthaldoxime-phenoxyacetic acid (Elkan, Abstr., 1887, 259),

NOH:CH·C$_6$H$_4$·O·CH$_2$·COOEt ;
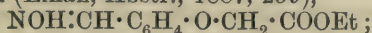
this melts at 80°. C. F. B.

An Isomeride of Diphenylene Bisulphide. By P. Genvresse (*Bull. Soc. Chim.*, 1897, [iii], **17**, 599—609. Compare Abstr., 1897, i, 240).—Phenylene bisulphide, (C$_6$H$_4$S)$_2$, and an isomeric compound are obtained by the action of sulphur on benzene in the presence of aluminium chloride. The diphenylene bisulphide may be removed by treating with boiling glacial acetic acid until the residue gives an emerald green colour with concentrated sulphuric acid ; the impure isomeride is then freed from excess of sulphur by washing with carbon bisulphide, and is dissolved in hot benzene, in which it is sparingly soluble and from which it separates on cooling in an amorphous condition. It melts at 295°, but begins to sublime even at lower temperatures, is sparingly soluble in hot benzene or chloroform, and is insoluble in most other solvents. Chromic acid oxidises it to *isodiphenylene disulphone*, $C_6H_4 \begin{array}{c} \diagup SO_2 \diagdown \\ \diagdown SO_2 \diagup \end{array} C_6H_4$, which has not been obtained in a crystalline form, but is colourless, melts above 360°, is non-volatile, and only sparingly soluble in benzene, and when heated with concentrated sulphuric acid at 200° is converted into a substance soluble in water.

Fuming nitric acid oxidises the isobisulphide, yielding a mixture of products which have not been separated.

Fuming sulphuric acid yields a colouring matter *isotrioxyphenylene bisulphide*, $C_6S_2H_4O_3$, when heated in sealed tubes at 120—125° with the isobisulphide; this compound is readily soluble in water or alcohol, giving red solutions, but is insoluble in benzene, chloroform, &c. In the solid state, it is brown, and with sulphuric acid gives a green solution; it may be obtained in a crystalline form from dilute sulphuric acid, but not from its aqueous or alcoholic solutions. Its aqueous solution, when mixed with a solution of sodium chloride, yields a brownish red precipitate, containing 70 per cent. of sodium chloride, and insoluble in alcohol. Sodium hydroxide turns the red, aqueous solution black, and a precipitate is slowly formed; a precipitate is also obtained with sodium carbonate, but no evolution of gas occurs. Barium hydroxide gives a dark brown precipitate, which, on adding an excess of hydroxide, becomes white; it is sparingly soluble in hot water, and its composition is represented by the formula $C_6S_2H_2O_3Ba$. The dark coloured precipitate can also be obtained in a crystalline form, and has the composition $(C_6S_2H_3O_3)_2Ba$.

A *triacetyl* derivative, $C_6S_2O_3HAc_3$, is obtained when the compound is boiled with acetic anhydride, but when the acetyl derivative is boiled with barium hydroxide, only one acetyl group is removed. The acetyl derivative forms a hard, black mass, soluble in water. The brown colouring matter gives azo-colours with aromatic amines.

<div align="right">J. J. S.</div>

Hydrazides and Azides of Sulphonic Acids. By Theodor Curtius and Ferdinand Lorenzen (*J. pr. Chem.*, 1898, [ii], **58**, 160—189. Compare this vol., i, 136).—The ethereal salts of aromatic sulphonic acids, $R \cdot SO_3H$, are completely hydrolysed on standing in the cold with hydrazine hydrate, the hydrazine first formed taking up water, with the production of the diammonium salt of the sulphonic acid, whereas the ethereal salts of sulphinic acids are not only hydrolysed, but decomposed by the reducing action of the diamide according to the following equation, $4PhSO_2Et + 3N_2H_5 \cdot OH = 2Ph_2S_2 + 4EtOH + 7H_2O + 3N_2$.

The hydrazides of the sulphonic acids can also be obtained by the action of hydrazine hydrate on the acid chloride; they reduce an ammoniacal solution of silver nitrate and Fehling's solution, and precipitate mercury from mercuric oxide. Iodine converts them into bisulphides and disulphoxides, but the latter could not be isolated, a similar reaction taking place when the sulphonehydrazides are heated. Like the hydrazides of the carboxylic acids, they are of a basic character, and condense with one molecule of an aldehyde or ketone. Acetic anhydride replaces one hydrogen of the hydrazine residue by an acetyl group, and nitrous acid converts them into the sulphon-azides, which, unlike the azides of carboxylic acids, are not changed by heating with water or alcohol; neither are they acted on by bromine, and only with great difficulty by alkalis.

Benzenesulphonehydrazide, $PhSO_2 \cdot NH \cdot NH_2$, crystallises from alcohol in large plates or prisms melting and giving off gas at 104—106°.

The *hydrochloride* separates from alcohol in fine needles melting, with evolution of gas, at 150—152°, and the *sodium* salt, $PhSO_2 \cdot NNa \cdot NH_2$, forms glistening plates.

Benzylidenebenzenesulphonehydrazine, $SO_2Ph \cdot NH \cdot N:CHPh$, formed by the action of benzaldehyde on the hydrazide, crystallises from dilute alcohol in colourless needles melting at 110—112°; the corresponding *acetone* [β-propylidene] derivative forms glistening leaflets melting at 143—145°, and the *acetyl* derivative crystallises in groups of glistening needles melting at 183—184°.

Dibenzenesulphonehydrazide, $SO_2Ph \cdot NH \cdot NH \cdot SO_2Ph$, produced by the interaction of benzenesulphonic chloride and benzenesulphonehydrazide, crystallises from alcohol or water in glistening needles melting and giving off gas at 228°. It reduces Fehling's solution and ammoniacal silver nitrate slowly in the cold, and is decomposed by iodine with evolution of nitrogen. Boiling dilute sulphuric acid decomposes it very slowly, but boiling alkalis decompose it readily with production of benzenesulphinic acid.

Benzenesulphonazide, SO_2PhN_3, is a yellowish oil which does not solidify when cooled, has a sweet odour, and when reduced with zinc dust and acetic acid is converted into benzenesulphonamide; it may be obtained by the action of nitric acid on benzenesulphonehydrazide.

Diammonium benzenesulphonate, $SO_3Ph \cdot N_2H_5$, obtained by the action of hydrazine hydrate on methylic benzenesulphonate, is a crystalline substance melting and decomposing at 175°. When further acted on by benzenesulphonic acid, it yields the *diammonium* salt, $N_2H_4(PhSO_3H)_2$, crystallising from alcohol in glistening leaflets, which begin to decompose when heated to 250° and are not completely melted at 275°.

The corresponding *diammonium* salt of benzenesulphinic acid, $N_2H_4(Ph_2SO_2H)_2$, crystallises from alcohol in glistening leaflets melting and decomposing at 139—141°.

β-Naphthylsulphonehydrazide crystallises from alcohol in colourless needles melting and evolving gas at 137—139°, and when boiled with dilute sulphuric acid, is converted into β-naphthylsulphinic acid and hydrazine sulphate. The *hydrochloride* forms tufts of needles melting at 148—150°, and the *sodium* salt crystallises from alcohol with 1EtHO in glistening leaflets, which do not melt when heated to 275°.

Benzylidene-β-naphthylsulphonehydrazine, $C_{10}H_7 \cdot SO_2 \cdot NH \cdot N:CHPh$, obtained by the action of benzaldehyde on the sulphonehydrazide, crystallises in colourless needles melting and giving off gas at 150—152°, and the corresponding *acetone* [β-propylidene] derivative forms glistening plates melting and decomposing at 156—158°.

Aceto-β-naphthylsulphonehydrazide, $C_{10}H_7 \cdot SO_2 \cdot NH \cdot NHAc$, prepared by the action of acetic anhydride on the sulphonehydrazide, forms colourless, glistening needles melting at 208—209°.

Di-β-naphthylsulphonehydrazide, $(C_{10}H_7 \cdot SO_2 \cdot NH)_2$, formed by the interaction of the sulphonehydrazide with β-naphthylsulphonic chloride, crystallises from alcohol in slender needles melting and decomposing at 215°. Dilute sulphuric acid converts it into β-naphthylsulphonic acid and hydrazine sulphate. The *sodium* salt is a yellow powder, not melting when heated to 275°.

β-*Naphthylsulphonazide*, $C_{10}H_7SO_2 \cdot N_3$, crystallises in white leaflets melting at 44—46°, but not exploding when heated to a higher temperature; when reduced with zinc dust and acetic acid, it is converted into β-naphthylsulphonamide.

Hydrazine hydrate acts on ethylic benzenesulphinate and methylic β-naphthylsulphinate, giving respectively phenylic bisulphide and β-naphthylic bisulphide, and not the sulphinehydrazides.   A. W. C.

4 : 4′-Diamidodiphenyl-3 : 3′-dicarboxylic Acid. By CARL BÜLOW and ULRICH VON REDEN (*Ber.*, 1898, **31**, 2574—2582).—This acid, $C_{12}H_6(NH_2)_2(COOH)_2$, is prepared by reducing orthonitrobenzoic acid in alkaline solution, and boiling the hydrazo-compound thus produced with concentrated hydrochloric acid. When it is dissolved in caustic soda, and the solution is shaken with benzoic chloride and kept cold meanwhile, 4 : 4′-*dibenzamidodiphenyl*-3 : 3′-*dicarboxylic acid*,

$$C_{12}H_6(NHBz)_2(COOH)_2,$$
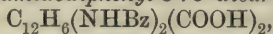
melting at 302—304°, is formed (the *ammonium* salt crystallises with $2H_2O$) ; with acetic anhydride instead of benzoic chloride, the *diacetamido*-compound is formed; this melts at about 300°, and is converted into benzidine when it is boiled in glycerol solution. When the acid is dissolved in dilute hydrochloric acid and treated with sodium nitrite, and the hydrochloride formed is repeatedly dissolved in water and precipitated with a mixture of alcohol and ether, yellow 4 : 4′-*tetrazodiphenyl*-3 : 3′-*dicarboxylic acid*,

$$C_{12}H_6(N{:}N \cdot OH)_2(COOH)_2 + 2H_2O,$$
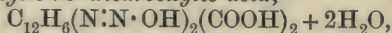
is obtained, and this, if boiled with 1 per cent. sulphuric acid, yields 4 : 4′-*dihydroxydiphenyl*-3 : 3′-*dicarboxylic acid*,

$$C_{12}H_6(OH)_2(COOH)_2,$$
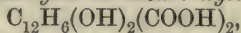
which melts at 302—305°, and yields 4 : 4′-dihydroxydiphenyl when heated with lime. When heated with bromine in hydrobromic acid solution, the tetrazo-acid yields a perbromide from which, by means of ammonia, greyish-green 4 : 4′-*disdiazoimidodiphenyl*-3 : 3′-*dicarboxylic acid*, $C_{12}H_6(N_3)_2(COOH)_2$, decomposing at 165°, is obtained. Reduced by prolonged boiling with absolute alcohol, it yields diphenyl-3 : 3′-dicarboxylic acid, from which diphenyl can be obtained by heating with lime ; the latter acid forms a *methylic* and an *ethylic* salt, melting at 100—102° and 68° respectively, when it is dissolved in the corresponding alcohol and the solution is saturated with hydrogen chloride. When reduced with sodium sulphite solution, the tetrazo-acid yields *diphenyl*-4 : 4′-*dihydrazine*-3 : 3′-*dicarboxylic acid*, $C_{12}H_6(NH \cdot NH_2)_2(COOH)_2$, which is greyish to reddish-white, carbonises without melting when heated, and condenses with acetone at 40—50° to form the dark green *disacetonediphenyl*-4 : 4′-*dihydrazone*-3 : 3′-*dicarboxylic acid*, $C_{12}H_6(NH \cdot N{:}CMe_2)_2(COOH)_2$, melting at 265—267°. With phenol in strong caustic soda solution, the tetrazo-acid condenses to form the red 4 : 4′-*disphenolazodiphenyl*-3 : 3′-*dicarboxylic acid*, $C_{12}H_6(N{:}N \cdot C_6H_4 \cdot OH)_2(COOH)_2$; with ethylic acetoacetate in aqueous sodium acetate solution, it gives 4 : 4′-*disethylic acetoacetate-azodiphenyl*-3 : 3′-*dicarboxylic acid*,

$$C_{12}H_6(N{:}N \cdot CHAc \cdot COOEt)_2(COOH)_2 + H_2O,$$
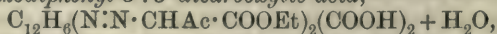
melting at 275—278° ; with ethylic malonate in the presence of dilute alcohol and sodium acetate, it yields, after crystallisation of the

product from alcohol, brownish-yellow *ethylic* 4 : 4'-*disethylic mesoxalate-dihydrazonediphenyl*-3 : 3'-*dicarboxylate*,

$$C_{12}H_6[N\cdot N\colon C(COOEt)_2]_2(COOEt)_2 + 2H_2O,$$
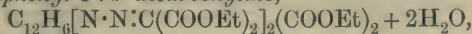
which melts at 257°. C. F. B.

Parahydroxyphenylphthalide, and its Conversion into Derivatives of Anthracene. By AUGUSTIN BISTRZYCKI and D. W. YSSEL DE SCHEPPER (*Ber.*, 1898, **31**, 2790—2802).—The hydroxyphenylphthalide, $CO{<}{\stackrel{-O-}{C_6H_4}}{>}CH\cdot C_6H_4\cdot OH$, previously described (Abstr., 1894, i, 600), yields *para*methoxyphenylphthalide (Nourrisson, Abstr., 1886, 1029) when methylated, and so must itself be a *para*-hydroxy-compound ; similar conclusions may be drawn as to the constitution of the other substances described at the same time.

When parahydroxyphenylphthalide is reduced in alkaline solution by boiling with zinc dust, it yields 4-*hydroxydiphenylmethane*-2'-*carboxylic* acid, $COOH\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot OH$, which melts at 145—146° ; its anhydrous *silver* salt was analysed. When it is dissolved in strong sulphuric acid at a temperature not exceeding 30°, and the solution is poured into water, the product is 2-*hydroxyanthranol*,

$$C_6H_4{<}{\stackrel{C(OH)}{\underset{CH-}{|}}}{>}C_6H_3\cdot OH;$$
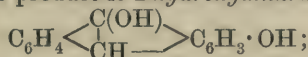
this melts at 221°, and forms a *diacetyl* derivative melting at 141—142° ; the latter, when oxidised with chromic acid in acetic acid solution, yields a product identical with β-acetoxyanthraquinone.

Metacresylphthalide yields a similar series of products. 4-*Hydroxy-2-methyldiphenylmethane*-2'-*carboxylic acid*,

$$COOH\cdot C_6H_4\cdot CH_2\cdot C_6H_3Me\cdot OH,$$
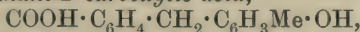
melts at 168—169° ; its anhydrous *barium* salt was analysed. 2-*Hydroxy-4-methylanthranol*, $C_6H_4{<}{\stackrel{C(OH)}{\underset{CH-}{|}}}{>}C_6H_2Me\cdot OH$, melts at 224°, its *diacetyl* derivative at 172—173°. 2-*Acetoxy-4-methylanthraquinone*, $C_6H_4{<}{\stackrel{CO}{\underset{CO}{}}}{>}C_6H_2Me\cdot OAc$, melts at 134—135°, is yellow, and, when hydrolysed with alcoholic potash, yields the 2-*hydroxy*-compound, which is yellow and melts at 299—300°, beginning to sublime at about 200°.

4 : 5' : 6'-*Trimethoxybenzoyl*-2'-*benzoic acid*,

$$COOH\cdot C_6H_2(OMe)_2\cdot CO\cdot C_6H_4\cdot OMe,$$
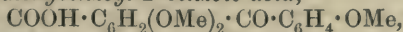
formed when hemipinic anhydride is heated in benzene solution with anisoil and aluminium chloride and the product treated with hydrochloric acid, melts at 215—216° ; its anhydrous *silver* salt was analysed. When reduced with zinc dust in alkaline solution, it yields *paramethoxyphenylpseudomeconine*, $CO{<}{\stackrel{-O-}{C_6H_2(OMe)_2}}{>}CH\cdot C_6H_4\cdot OMe$, which melts at 111—113°. With zinc dust and hydrochloric acid in acetic acid solution, 4 : 5' : 6'-*trimethoxydiphenylmethane*-2'-*carboxylic acid*, $COOH\cdot C_6H_2(OMe)_2\cdot CH_2\cdot C_6H_4\cdot OMe$, melting at 122—124°, is obtained ; strong sulphuric acid converts this into 2 : 3' : 4'-*trimethoxy-dihydroanthrone*, $C_6H_2(OMe)_2{<}{\stackrel{CO-}{\underset{CH_2}{}}}{>}C_6H_3\cdot OMe$, which melts at

169—170°, and is oxidised by chromic acid in acetic acid solution to 2 : 3′ : 4′-*trimethoxyanthraquinone*, $C_6H_2(OMe)_2{<}^{CO}_{CO}{>}C_6H_3 \cdot OMe$, which is yellow, melts at 225°, and yields flavopurrin when heated with aluminium chloride at 210°.

Dinitroparahydroxyphenylphthalide, $CO{<}^{-O-}_{C_6H_4}{>}CH \cdot C_6H_2(NO_2)_2 \cdot OH$ [$(NO_2)_2 : OH = 3 : 5 : 4$, probably], obtained by treating parahydroxy phenylphthalide with the theoretical quantity of nitric acid (sp. gr. $= 1·50$) in concentrated acetic acid solution, is yellow, and melts at 187°. *Amidoparahydroxyphenylphthalide*,

$$CO{<}^{-O-}_{C_6H_4}{>}CH \cdot C_6H_3(NH_2) \cdot OH \quad [NH_2 : OH = 3 : 4, \text{ probably}],$$
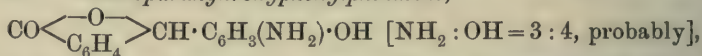
is obtained by reducing the corresponding nitro-compound (Abstr., 1894, i, 600) with tin and hydrochloric acid; it is yellowish, and melts at 229—230°.

When a mixture of phthalaldehydic acid and 1-naphthol is stirred into 73 per cent. sulphuric acid at 0°, the product is 4-*hydroxynaphthylphthalide*, $CO{<}^{-O-}_{C_6H_4}{>}CH \cdot C_{10}H_6 \cdot OH$; it melts at 222—223°. An isomeric substance [$OH = 2$ (?)], obtained in a similar way from 2-naphthol, melts at 234—235°.   C. F. B.

Electrolytic Reduction of Aldehydes and Ketones. By Hugo Kauffmann (*Zeit. Elektrochem.*, 1898, 4, 461. Compare Abstr., 1896, i, 649).—Benzaldehyde, dissolved in alcoholic caustic soda, gives a good yield of the two hydrobenzoins when quickly reduced by means of a fairly large current. Other aldehydes and ketones behave similarly, acetophenone giving acetophenonepinacone, and the ketone,

$$CO[C_6H_4 \cdot N(CH_3)_2]_2,$$
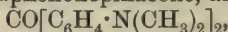
the corresponding benzhydrol.

In acid solution, the reaction takes place less smoothly, benzaldehyde giving large quantities of resinous products. Benzil (10 grams), dissolved in boiling alcohol (150 c.c.) and 10 per cent. solution of sodium hydroxide (30 c.c.), and electrolysed for 6 hours at 70—80° with 2—3 ampères, gives, besides benzoic and benzilic acids, symmetrical *tetraphenylerythritol* or *benzoinpinacone*,

$$OH \cdot CHPh \cdot CPh(OH) \cdot CPh(OH) \cdot CHPh \cdot OH,$$
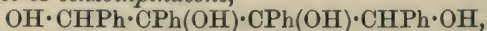
the yield of the latter being about 10 per cent. of the benzil used. This substance melts at about 235°, crystallises from alcohol in slender needles, and is most readily soluble in alcohol containing some alkali, but very sparingly in other solvents. When evaporated, the mother liquor of the benzoinpinacone deposits thick crystals which, after recrystallisation from chloroform, melt at 175° and have the composition $C_{28}H_{26}O_3$. Benzoinpinacone was also obtained by the electrolytic reduction of benzoin; when heated at 235—240° in a *vacuum*, it loses $1H_2O$, forming benzoin. With acetic chloride, it loses water and forms a diacetyl compound, probably $O{<}^{CHPh \cdot CPh \cdot OAc}_{CHPh \cdot CPh \cdot OAc}$; this crystallises from alcohol in white plates melting at 198°.

The substance $C_{28}H_{26}O_3$ does not undergo the pinacone decomposi-

tion ; it forms a monacetyl compound, losing $1H_2O$ at the same time. The author considers that its constitution is probably
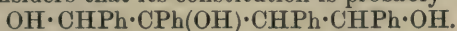
$$OH \cdot CHPh \cdot CPh(OH) \cdot CHPh \cdot CHPh \cdot OH.$$ T. E.

Condensation of Mandelonitrile with Phenols. By AUGUSTIN BISTRZYCKI and HUGO SIMONIS (*Ber.*, 1898, **31**, 2812—2813).— a-Hydroxydiphenylacetolactone can be prepared directly from commercial mandelonitrile by acting on the latter with sulphuric acid and phenol, and this greatly lessens the cost of production.

Neither the lactone nor the sodium salt of the acid appears to produce any definite physiological effect on dogs.   A. H.

γ-Lactones of Phenolic Acids. By GUSTAV CRAMER (*Ber.*, 1898, **31**, 2813—2821).

I. *Derivatives of Orthohydroxydiphenylacetolactone.—Ethylic orthohydroxydiphenylacetate*, $OH \cdot C_6H_4 \cdot CHPh \cdot COOEt$, obtained by the action of alcoholic hydrogen chloride on the lactone, crystallises in stellate groups of prisms melting at 104—106°. γ-Lactones of alcoholic acids, on the other hand, are usually converted into chloroacids by this treatment. *Orthohydroxydiphenylacetamide* is obtained by the action of ammonia on the lactone, and crystallises in slender needles melting at 161—162°. When it is heated at 180°, it is converted into the lactone. The corresponding *methylamide*,

$$OH \cdot C_6H_4 \cdot CHPh \cdot CO \cdot NHMe,$$
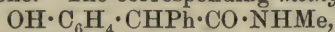
prepared by the action of methylamine on the lactone, crystallises in small needles melting at 180—182°; the *anilide*, obtained in a similar manner, crystallises in lustrous, white plates melting at 143—146°. *Orthohydroxydiphenylamidoacetamide*,

$$OH \cdot C_6H_4 \cdot CPh(NH_2) \cdot CO \cdot NH_2,$$
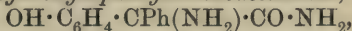
is formed by the action of aqueous ammonia on orthohydroxydiphenylbromacetolactone, and melts and decomposes at 150—151°. When it is boiled with hydrochloric acid, it is converted into the *orthohydroxydiphenylglycocine hydrochloride*, which melts at 275—278°. The corresponding *acid* crystallises in very hygroscopic needles melting at 210—215°, and probably has the constitution $OH \cdot C_6H_4 \cdot CPh \underset{CO}{\overset{NH_3}{<}} O$.

It follows from this that the additive product obtained by the action of ammonia on the bromolactone is a true hydroxyamide and does not contain the lactone ring. *Orthohydroxydiphenylacetamidoacetolactone*, $NHAc \cdot CPh \underset{-CO}{\overset{C_6H_4}{<}} O$, obtained by the action of acetic anhydride and sodium acetate on the hydrochloride of orthohydroxydiphenylglycocine, crystallises in slender, lustrous needles melting at 225—228°.
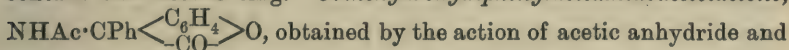
II. *Derivatives of Phenylparacresylacetolactone.—Phenylparacresylacetamide*, $OH \cdot C_6H_3Me \cdot CHPh \cdot CO \cdot NH_2$, crystallises in stellate groups of lustrous prisms and melts at 139—140°. *Phenylparacresylbromacetolactone*, $CPhBr \underset{-CO}{\overset{C_6H_3Me}{<}} O$, forms well developed, tabular monosymmetric crystals $[a : b : c = 1 \cdot 8482 : 1 : 2 \cdot 1060 ; \beta = 85° 13']$. *Phenylparacresylamidoacetamide*, $OH \cdot C_6H_3Me \cdot CPh(NH_2) \cdot CO \cdot NH_2$, forms lustrous crystals melting at 146—148°. *Phenylparacresylglycocine*, $OH \cdot C_6H_3Me \cdot CPh(NH_2) \cdot COOH$, which is almost insoluble in any of
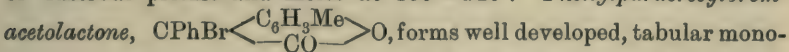
the ordinary solvents, melts at 190—192°; the *hydrochloride* readily loses hydrogen chloride if left in a desiccator. *Phenylparacresylacetamidoacetolactone*, $NHAc \cdot CPh <^{C_6H_3Me}_{-CO-}> O$, crystallises in lustrous needles melting at 214—216°. *Phenylparacresylethoxyacetolactone*, $OEt \cdot CPh <^{C_6H_3Me}_{CO-}> O$, crystallises in lustrous prisms melting at 122°. *Phenylparacresylethoxyacetic* acid, $OH \cdot C_6H_3Me \cdot CPh(OEt) \cdot COOH$, crystallises in slender needles melting at 131—134°, and its *amide* in small needles melting at 103—105°.

III. *Derivatives of Phenylmetacresylacetolactone.*—*Phenylmetacresylacetamide* crystallises in lustrous prisms melting at 163—166°. *Phenylmetacresylbromacetolactone* forms pale yellow, lustrous plates melting at 96—97°. *Phenylmetacresylethoxyacetolactone* crystallises in lustrous prisms melting at 91—93°.   A. H.

Condensation of Mandelic Acid with β-Naphthol, Resorcinol, and Orcinol. By HUGO SIMONIS (*Ber.*, 1898, 31, 2821—2830).— Phenyl-β-hydroxynaphthylacetolactone is best prepared by the action of mandelonitrile on β-naphthol. The *basic barium* salt, $C_{18}H_{12}O_3Ba$, crystallises with $3H_2O$ in small, soluble prisms, whilst the *normal* salt, $(C_{18}H_{13}O_3)_2Ba + 2H_2O$, is sparingly soluble, and crystallises in long, thread-like needles. *Phenyl-β-hydroxynaphthylbromacetolactone*, $CPhBr <^{C_{10}H_6}_{-CO-}> O$, produced by the action of bromine on the lactone, forms well-developed, greenish-yellow, monosymmetric crystals [$a:b:c = 1·2894 : 1 : 0·480$; $\beta = 91° 30'$], and melts at 121°. *Phenyl-β-hydroxynaphthylmethoxyacetolactone*, $OMe \cdot CPh <^{C_{10}H_6}_{-CO-}> O$, obtained by the action of methylic alcohol on the foregoing compound, crystallises in yellow prisms melting at 136°. *Phenyl-β-hydroxynaphthylethoxyacetolactone* forms colourless crystals melting at 145°, and is accompanied by two deep yellow substances melting at 187° and 223° respectively. The corresponding acid forms a *basic barium* salt, $C_{20}H_{16}O_4Ba$, as well as a *normal* salt, both of which are sparingly soluble in water. *Phenyl-β-hydroxynaphthylbenzyloxyacetolactone*,

$$CH_2Ph \cdot O \cdot CPh <^{C_{10}H_6}_{-CO-}> O,$$
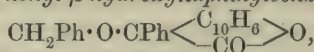
obtained by the action of benzylic alcohol on the bromo-compound, forms colourless crystals and melts at 181°, whilst the corresponding *phenoxy*-derivative melts at 160°.

Mandelic acid reacts with resorcinol in presence of sulphuric acid to form two isomeric lactones. *Phenylresorcylacetolactone* melts at 133°, and probably has the constitution $^{CH:CH \cdot C \cdot CHPh}_{OH \cdot C:CH - C - O} > CO$. It forms tabular asymmetric crystals [$a:b:c = 0·6007 : 1 : 0·7010$; $\alpha = 75° 42'$; $\beta = 116° 19'$; $\gamma = 108° 16'$].

The isomeric compound, *isophenylresorcylacetolactone*, melts at 125°, and probably has the constitution $^{CH:C(OH) \cdot C \cdot CHPh}_{CH:CH - C - O} > CO$. The crystals belong to the rhombic system [$a:b:c = 0·895 : 1 : 0·784$].
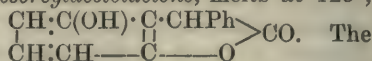
Both lactones yield bromo-derivatives, that of the normal lactone melting at 145°, and that of the isolactone at 142°. *Dibromophenyl-resorcylacetolactone*, $C_{14}H_8O_3Br_2$, is obtained from the lactone melting at 183°, and probably has the constitution $CO\!\!<^{CPhBr}_{-O-}\!\!>C_6H_2Br\cdot OH$.

Orcinol, like resorcinol, yields two isomeric lactones. *Phenylorcylacetolactone* crystallises in slender needles melting at 155°. The *isolactone* melts at 172°. *Monobromophenylorcylacetolactone* forms brownish crystals melting at 185°, whilst the *dibromo-lactone* melts at 205°.

A. H.

A Periodide of Triphenylbromomethane. By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1898, **20**, 790).—On mixing solutions, in benzene or carbon bisulphide, of triphenylbromomethane and excess of iodine, a *periodide*, CPh_3BrI_4, crystallises out; after recrystallisation from benzene or carbon bisulphide, it melts at 121—122°. The periodide may be obtained in bluish-green, iridescent, hexagonal prisms or in small needles. On two occasions, the unusual phenomenon of the formation of hollow crystals was observed, the canal apparently coinciding with the longitudinal axis of the crystal. The author points out that all periodides hitherto described are those of metallic salts or of bases, whereas triphenylbromomethane is not a base.

G. W. F. H.

Tetraphenylmethane. By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1898, **20**, 773—780).—This paper is a revision of the author's work on tetraphenylmethane (Abstr., 1897, i, 623). Triphenylmethane is brominated, and the triphenylbromomethane produced treated with phenylhydrazine, when it yields triphenylmethanehydrazobenzene; this, when oxidised with nitrous anhydride, gave triphenylmethane-azobenzene melting at 110—112°, which, on heating at 110—120°, evolves nitrogen, forming tetraphenylmethane, the yield being, however, very poor. Tetraphenylmethane crystallises from benzene in white, glistening needles.

That tetraphenylmethane is really formed, is indicated, not only by the analysis, but by a cryoscopic determination of the molecular weight; moreover, the substance is readily and completely converted into a tetranitro-derivative melting at 275°; this does not yield a sodium derivative by the action of sodium ethoxide, whereas the nitrophenylmethane derivatives, $CH_2[C_6H_3(NO_2)_2]_2$, $NO_2\cdot C_6H_4\cdot CH_2\cdot CN$, $CH(C_6H_4\cdot NO_2)_3$, which still contain hydrogen attached to the methane carbon atom, readily yield sodium derivatives. Tetranitrotetraphenylmethane appears to be reduced by zinc dust and acetic acid to leucopararosaniline.

G. W. F. H.

Constitution of Phthalyl-Green. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1897, **125**, 1153—1156. Compare Abstr., 1881, 587, and 1898, i, 483). The colouring matter produced by the condensation of phthalyl tetrachloride and dimethylaniline is identical with O. Fischer's phthalyl-green. There are many points of resemblance between this compound and malachite-green, and the authors put forward the formula,

$$NMe_2\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CCl(C_6H_4\cdot NMe_2)_2,$$
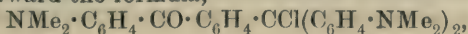
as being most in accordance with the reactions of the former substance ; in other words, phthalyl-green is malachite-green containing the radicle, $NMe_2 \cdot C_6H_4 \cdot CO$, introduced into an ortho-position in the non-substituted phenyl group. The leuco-base obtained from such a colouring matter should have the formula,

$$NMe_2 \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot CH(C_6H_4 \cdot NMe_2)_2,$$
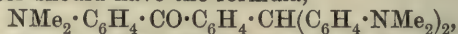
which is in agreement with O. Fischer's analytical results. Rosenstiehl has shown that the basic colouring matters of the triphenylmethane series containing n atoms of amidic nitrogen are capable of combining with $(n + 1)$ molecules of hydrochloric acid to form polyhydrochlorides, of which pararosaniline tetrahydrochloride, $CCl(C_6H_4 \cdot NH_2, HCl)_3$, may be taken as the type.

Phthalyl-green behaves like pararosaniline, and forms a tetrahydrochloride. This compound, although containing four chlorine atoms ought not to combine with 2 molecules of platinic chloride, since the formation of a platinochloride is due only to the presence of quinquevalent nitrogen atoms. It might be expected, however, that 2 molecules of the tetrahydrochloride would combine with 3 molecules of platinic chloride. The platinochloride obtained by the addition of platinic chloride to a solution of the colouring matter in concentrated hydrochloric acid has the formula $(C_{32}H_{34}N_3OCl)_2,3H_2PtCl_6$.   G. T. M.

Mercurial Compounds of β-Naphthol. By EUGEN BAMBERGER (*Ber.*, 1898, **31**, 2624—2626).—The author has obtained with β-naphthol results similar to those described by Dimroth (this vol., i, 54) in the case of phenol. *β-Hydroxynaphthyl-1-mercuric acetate*, $OH \cdot C_{10}H_6 \cdot Hg \cdot OAc$, is made by adding β-naphthol (13·2 grams) to a clear solution of mercuric oxide (20 grams) in hot acetic acid (520 c.c.) ; it separates at once as a heavy, crystalline precipitate, and can be purified by recrystallisation from hot acetic acid. It crystallises in white, shining needles, and, when quickly heated, melts and decomposes at 185° ; it is sparingly soluble in most of the usual media, but dissolves readily in soda, and is reprecipitated on addition of acetic acid ; on addition of ammonium sulphide to its aqueous solution, a voluminous, yellow precipitate is produced which blackens when the liquid is heated, mercuric sulphide being formed. The mercury is very loosely attached to the naphthol nucleus, and the union is destroyed by the addition of soda or of diazotates, β-naphthol being formed in the first case, and phenolazonaphthols being produced in the second.

A. L.

Synthetical Isoborneols; their Identity with the Fenchylic Alcohols. By GUSTAVE BOUCHARDAT and J. LAFONT (*Compt. rend.*, 1898, **126**, 755—757.)—Synthetically prepared dextrorotatory isoborneol, obtained by the authors by the action of certain acids on lævorotatory turpentine, consists of a mixture of the dextrorotatory and inactive fenchylic alcohols ; these, on oxidation, give rise to lævorotatory and inactive fenchone respectively. The former is the optical antipode of the dextrorotatory fenchone obtained from oil of fennel ; both compounds have the same crystalline form and melting point, and their specific rotations are equal in magnitude but opposite in sign. The corresponding fenchone oximes bear similar relations to

each other, and when equal weights of them are mixed together, in ethereal solution, a racemoid form, melting at 154—156°, is obtained on evaporation. When lævorotatory fenchone is reconverted into dextrorotatory fenchylic alcohol by reduction with alcoholic potash or sodium and alcohol, the optical activity of the substance is less than it was originally.   G. T. M.

Beetroot-resin Acid. By KARL ANDRLÍK and EMIL VOTOCEK (*Chem. Centr.*, 1898, i, 621—622; from *Neu. Zeit. Rüb.-Zuck.-Ind.*, **40**, 39—44).—According to the authors, the substance obtained from the scum formed in the first treatment of the sugar liquors with lime and carbonic anhydride is not isocholesterol, as Kollrepp supposed, but a kind of resin to which they give the name beetroot-resin acid. It is prepared by treating the scum with dilute hydrochloric acid and extracting the dry, insoluble material with alcohol. The scum on the waste water of the factory, the deposits in the heating apparatus for the diffusion process, and the diffused juice also contain this substance. It crystallises from alcohol in colourless, silky needles, melts at 299—300°, has a specific rotatory power $[\alpha]_D = +74\cdot4°$ at 20°, is insoluble in water, easily soluble in boiling alcohol, amylic alcohol, and isobutylic alcohol, and less soluble in methylic than in ethylic alcohol. It dissolves easily in glacial acetic acid, but the solution, on evaporation, does not yield the original compound. When heated above the melting point, it sublimes and partially decomposes, forming a liquid and a crystalline sublimate; the latter melts and chars at 241°. The resin-acid has the composition $C_{22}H_{36}O_2$, and crystallises with $1H_2O$. The colour reactions with sulphuric acid and acetic anhydride are like those of abietic acid, vitine, ursone, gentiol, cholesterol, and many resin-acids. The sodium and potassium salts were prepared.   E. W. W.

Aloins. By EUGÈNE LÉGER (*Compt. rend.*, 1898, **127**, 234—236. Compare Abstr., 1898, i, 445).—*Trichlorobarbaloin*, $C_{16}H_{13}Cl_3O_7 + H_2O$, obtained by the action of potassium chlorate on a solution of barbaloin in concentrated hydrochloric acid, crystallises from alcohol of 90 per cent. in monoclinic, rhomboidal tablets $[a : b : c = 1\cdot5448 : 1 : 1\cdot3880]$. Unlike barbaloin, it dissolves in sodium carbonate solution, but it does not displace carbonic acid. When heated in sealed tubes with acid chlorides, it yields *triacetyltrichlorobarbaloin*, which crystallises in very thin, microscopic, rhomboidal lamellæ, and *tribenzoyltrichlorobarbaloin*, an amorphous compound very soluble in acetone, but almost insoluble in alcohol. Under different conditions, barbaloin itself yields only a diacetyl or dibenzoyl derivative, but there can be no doubt that barbaloin contains three hydroxyl groups, which have a phenolic function, for it gives an olive-green coloration with ferric chloride, dissolves in alkali hydroxides, but not in the carbonates, and when heated with sodium hypobromite in excess, yields carbonic and oxalic acids and carbon tetrachloride.

Isobarbaloin, $C_{16}H_{16}O_7$, is found in the last fractions of the crystallisation of a mixture of aloins. It crystallises from methylic alcohol in opaque nodules, composed of elongated and truncated, micro-

scopic lamellæ which contain $3H_2O$ and are efflorescent; when crystallised from water, it forms pale yellow, prismatic needles which contain $2H_2O$. With benzoic chloride in presence of pyridine, it yields *dibenzoylisobarbaloin*, very similar to the corresponding barbaloin derivative. *Trichlorisobarbaloin*, obtained by the action of potassium chlorate and hydrochloric acid, forms brilliant yellow, prismatic needles; when heated in sealed tubes with acetic chloride, it yields a crystallisable triacetyltrichlorisobarbaloin. *Tribromisobarbaloin* is identical with the compound hitherto described as tribromobarbaloin.

The relative proportions of barbaloin and isobarbaloin vary greatly in aloes from different localities.   C. H. B.

Kosin. By GIROLAMO DACCOMO and GIOVANNI MALAGNINI (*L'Orosi*, 1897, **20**, 361—371).—Commercial kosin, obtained from the flowers of *Hagenia abyssinica*, melts at 147—149·5°, and appears to be a mixture of at least two substances, since, on fractional dissolution in, and crystallisation from, alcohol, it yields products having melting points ranging from 105° to 161°. The portion of highest melting point is the principal constituent of the commercial substance, and resembles in its properties the kosin described by Flückiger and Buri; it crystallises in long, yellow needles, which are insoluble in water but more or less soluble in organic solvents, and dissolves in alkalis, yielding solutions from which it is reprecipitated unchanged on the addition of acids. Its solutions give a violet coloration with ferric chloride, reduce an ammoniacal solution of silver nitrate, and react with phenylhydrazine to form resinous products, and probably a hydrazone; no reaction takes place, however, with Fehling's solution or with hydroxylamine. This substance, to which the term "kosin" is properly restricted, is shown by analysis and by cryoscopic molecular weight determinations (found, 411; theory, 402) to be more accurately represented by the formula $C_{22}H_{26}O_7$, than by the formula $C_{31}H_{38}O_{10}$, proposed by Flückiger and Buri.

Triacetylkosin, $C_{22}H_{23}Ac_3O_7$, obtained by the action of acetic anhydride on kosin, crystallises from alcohol in small, colourless needles. The corresponding *benzoyl* derivative, obtained by the action of benzoic chloride on a solution of kosin in caustic potash, forms small, almost colourless crystals. The analyses of these compounds and cryoscopic molecular weight determinations are in accordance with the formula proposed for kosin by the authors.

Kosin readily undergoes oxidation in alkaline solution, with the formation of isobutyric acid and complex resinous substances. With potassium permanganate, oxalic acid is also obtained, whilst when bromine or iodine is employed, bromoform and iodoform are respectively produced. Kosin resembles filicic acid in many respects, but differs from it in not reacting with Fehling's solution or with hydroxylamine. The existence of three hydroxyl groups in the molecule of kosin is shown by the formation of the acetyl and benzoyl derivatives, whilst its behaviour with phenylhydrazine and with oxidising agents indicates the presence of a ketonic nucleus to which an isopropyl group is probably attached.   N. L.

Strophanthin. By Leopold Kohn and Victor Kulisch (*Monatsh.*, 1898, **19**, 385—402. Compare Abstr., 1898, i, 326 and 327).—The strophanthin which the authors have described (Abstr., 1898, i, 329) is not identical with Feist's preparation (*ibid.*). The seeds from which they obtained the principle were those of *Strophanthus Kombé* or *S. hispidus*, probably the former, as they appear to be identical with those employed by Feist, and the isolation of the substance was achieved by Arnaud's process (Abstr., 1888, 1310).

The seeds, carefully freed from the adherent hairs, were powdered as finely as possible, washed in a Soxhlet's apparatus with light petroleum, and extracted with 70 per cent. alcohol. To the alcoholic extract, basic lead acetate and lead hydroxide were added, the lead being subsequently eliminated from the filtered liquid by means of hydrogen sulphide ; the filtrate was then evaporated in a vacuum, and the crude strophanthin so obtained purified by repeated crystallisation from water ; it appears to be identical with Merck's "crystallised strophanthin," which is obtained from *Strophanthus hispidus.*

The substance is inactive ; it is very hygroscopic and, when damp, melts at 100° ; the melting point of the anhydrous substance is very uncertain, but lies near 179°.

The authors' analyses gave numbers in close agreement with those obtained by Arnaud, but it is as yet uncertain which of the formulæ, $C_{31}H_{48}O_{12}$ or $C_{38}H_{58}O_{15}$, represent the true composition of the substance.

Strophanthin appears to contain a methoxy-group ; a determination by Zeisel's method gave a methoxyl content = 3·77—3·4 per cent., a number which points to the second of the above formulæ as being the correct one.

Acetylstrophanthin, $C_{31}H_{44}O_8(OAc)_4$, or $C_{38}H_{53}O_{10}(OAc)_5$, is made by heating strophanthin with acetic anhydride and anhydrous sodium acetate, and can be purified by recrystallisation from hot alcohol ; it forms very long, slender, colourless microscopic needles, melts at 236—238°, and is insoluble in water.

Strophanthidin crystallises from hot alcohol in beautiful, slender, white needles which aggregate to form silky leaflets. It melts at 195°, does not dissolve in water, but is very hygroscopic ; it cannot be dried at 100°, as it suffers slight decomposition at that temperature. It has the formula $C_{19}H_{28}O_4$, or $C_{28}H_{40}O_6$, but, like strophanthin, its methoxyl content is too low, and is lower even than that required by the latter formula. A. L.

Action of Cinnamaldehyde on Phenyltoluidoacetonitrile. By Wilhelm von Miller and Josef Plöchl (*Ber.*, 1898, **31**, 2718—2720). —In distinction from the behaviour of aromatic aldehydes, which yield two indifferent isomeric compounds with anilido-derivatives or with amido-nitriles, aliphatic aldehydes yield but one indifferent product (compare this vol., i, 127). In order to examine the behaviour of unsaturated aldehydes under similar conditions, the action of cinnamaldehyde on phenyltoluidoacetonitrile has been studied.

Diphenyltolylpyrroline, $\begin{array}{c}\text{CH:CPh}\\|\\\text{CH:CPh}\end{array}\Big>\text{N·}C_6H_4\text{Me}$, obtained by heating

phenyltoluidoacetonitrile with cinnamaldehyde and potash in alcohol, crystallises from alcohol in lustrous prisms, and melts at 181°; it arises from the union of the aldehyde and nitrile in molecular proportion, involving elimination of water and hydrogen cyanide, also in molecular proportion. The additive *compound*, $CHPh:CH \cdot CH(OH) \cdot CPh(CN) \cdot NH \cdot C_6H_4Me$, melts and decomposes at 175°; it doubtless represents an intermediate stage in the production of diphenyltolylpyrroline, which is generated along with hydrogen cyanide when the substance is heated.

M. O. F.

Distillation of Mixtures of Pyridine and Aliphatic Acids. By GUSTAVE ANDRÉ (*Compt. rend.*, 1897, **125**, 1187—1189).—Chemical combination evidently occurs when formic, acetic, and propionic acids are mixed with pyridine, for an appreciable amount of heat is developed, but when the mixture is titrated with standard baryta, using turmeric or phenolphthalein as indicators, the acidity is found to be equal to the whole amount of acid added. After six fractionations of a mixture of propionic acid and pyridine, in molecular proportion, a distillate is obtained boiling at 150—151° under a pressure of 760 mm. This liquid has approximately the composition $2C_3H_6O_2, C_5H_5N$, and it boils 11° higher than propionic acid and 37° higher than pyridine. When boiled under reduced pressure, the mixture has no definite boiling point, and the first distillates contain more pyridine than is required by the above formula.

A mixture of acetic acid and pyridine behaves in a similar manner; the least volatile portion boils at 139—140° under 760 mm., and its composition corresponds with $3C_2H_4O_2, 2C_5H_5N$. When fractionated, this portion is gradually dissociated; ebullition always commences at 100°, and the temperature rises slowly to 139—140°; when distilled under a pressure of 60 mm., it passes over unchanged at 74°, but under 20 mm. it is dissociated.

A mixture of pyridine and formic acid, in molecular proportion, after seven fractionations, yields a distillate boiling at 148—151° (760 mm.), of the composition $5CH_2O_2, 2C_5H_5N$; this mixture, when distilled under a pressure of 36 mm., boils at 74° without dissociation.

G. T. M.

Ammonio- and Pyridine Salts and Hydrates of Bivalent Metals. By FRITZ REITZENSTEIN (*Zeit. anorg. Chem.*, 1898, **18**, 253—304. Compare Abstr., 1895, i, 121; 1897, i, 380).—The author discusses the relations between the ammonium salts, hydrates, and pyridine compounds of metals. The repeated occurrence of the same type in the three series is most easily explained hy Werner's theory. The character of the acid residue which is combined with the metal becomes of more importance as the number of pyridine molecules increases; and the influence of the metallic atom varies in the inverse manner. The greatest number of pyridine molecules which can be combined is six, and this occurs in the compounds with $CuBr_2$, $CdBr_2$, and CdI_2. The greatest number of quinoline molecules is four, occurring in the compounds with $CuCl_2$ and $CoCl_2$. Isomerides of the

formula $=MeX_2 2Py$, which, according to Jörgensen's and Werner's theories, are possible, have not been obtained.

The author gives a table of all the known ammonium, pyridine, and quinoline salts and hydrates, and describes the following new compounds.

Monopyridine nickel chloride pentahydrate, $NiCl_2,C_5H_5N,5H_2O$, is obtained by exposing monopyridine nickel chloride to the air for 4—5 days.

Nickel chloride monopyridine hydrochloride, $NiCl_2,C_5H_5N,HCl$, is obtained by treating finely divided nickel chloride with pyridine, dissolving the product in concentrated hydrochloric acid, and evaporating the solution on the water-bath. It crystallises in flesh-coloured needles, deliquesces in the air, gives a green solution in water, and characteristic precipitates with potassium ferrocyanide and ferricyanide. When the mother liquors obtained in the preparation of this salt are evaporated, a compound is obtained which separates in blue crystals, and is probably a tetrahydrochloride compound.

Nickel chloride dipyridine hydrochloride, $NiCl_2,(C_5H_5N,HCl)_2$, was obtained on one occasion by dissolving nickel oxide in pyridine hydrochloride, and concentrating the solution on the water-bath, but the author was unable to obtain it again. The solution, on evaporation, first yields the salt $2NiCl_2,3C_5H_5N$, crystallising in greenish-yellow needles; on further concentration, it yields $NiCl_2,C_5H_5N$, then $NiCl_2,C_5H_5N,HCl$, and finally $NiCl_2,4C_5H_5N$, which crystallises from pyridine in bright blue needles.

Nickel sulphate tripyridine dihydrate, $NiSO_4,3C_5H_5N,2H_2O$, obtained by adding excess of pyridine to an aqueous solution of nickel sulphate, then adding alcohol and boiling, is a bluish-green, crystalline mass soluble in water, and gives a green precipitate with potassium ferrocyanide.

Cobalt chloride tetrapyridine, $CoCl_2,4C_5H_5N$, is obtained by heating a mixture of cobalt chloride and excess of pyridine hydrochloride in alcoholic solution; when dissolved in alcohol, it yields a blue compound, probably $CoCl_2,2C_5H_5N,2EtOH$, which quickly decomposes into the dipyridine compound.

Cobalt chloride monopyridine pentahydrate, $CoCl_2,C_5H_5N,5H_2O$, is obtained as a reddish, crystalline mass by allowing cobalt chloride monopyridine to remain exposed to the air for a few days.

Dicobalt chloride pentapyridine hydrochloride, $2CoCl_2,(C_5H_5N,HCl)_5$, obtained by heating the tetrapyridine compound dissolved in water with excess of hydrochloric acid, and also by the action of concentrated hydrochloric acid on a mixture of cobalt chloride and pyridine, is a dark blue, crystalline powder, and gives a red solution in water; when treated with silver nitrate, all the chlorine is precipitated.

Cobalt chloride dipyridine monohydrochloride, $CoCl_2,2C_5H_5N,HCl$, obtained by treating the preceding compound in alcoholic solution with the theoretical quantity of silver oxide, crystallises in dark blue crystals, melts at 155°, is soluble in cold water with a red coloration, and, when heated in the air-bath at 150° is converted into the basic chloride, $CoCl_2,CoO$. When treated with excess of silver oxide in alcoholic solution, it is converted into cobalt chloride dipyridine.

When cobalt chloride dipyridine is treated with ammonia and hydrochloric acid, a *salt* of the composition $CoCl_2,(C_5H_5NCl,NH_4Cl)_2,3H_2O$, is obtained, which crystallises from absolute alcohol in bright blue needles, darkens at 120°, melts at 128—130°, and when exposed to the air quickly turns red. The tetrapyridine and dipyridine compounds of cobalt chloride, when exposed to the air, take up water and give off pyridine in varying proportions according to the time of exposure, and compounds of the following composition were obtained, $CoCl_2,2C_5H_5N,2H_2O$; $CoCl_2,1\frac{1}{2}C_5H_5N,3\frac{1}{2}H_2O$, and
$$CoCl_2,3C_5H_5N,3H_2O.$$

Cobalt sulphate tripyridine dihydrate, $CoSO_4,3C_5H_5N,2H_2O$, obtained by treating an aqueous solution of cobalt sulphate with pyridine, separates in blood-red crystals, cannot be recrystallised from absolute alcohol or pyridine, is decomposed by warm water with precipitation of cobalt hydroxide, and, when treated with barium chloride, gives a quantitative precipitate of barium sulphate. When allowed to remain exposed to the air for a month, it is converted into the compound $CoSO_4,C_5H_5N,2H_2O$.

Cobalt nitrate, when heated with pyridine, yields a red compound, which can be recrystallised from absolute alcohol, smells strongly of pyridine, and is probably $Co(NO_3)_2,4C_5H_5N$.

The author was unable to obtain a compound of ferrous chloride with pyridine in aqueous solution. When solid ferrous chloride is shaken with pyridine, the *compound* $FeCl_2,3C_5H_5N,2H_2O$ is obtained ; this is a yellow, crystalline powder, has a strong odour of pyridine, is very easily decomposed, and is slightly soluble in water.

Ferrous sulphate tripyridine dihydrate, $FeSO_4,3C_5H_5N,2H_2O$, obtained in brownish-yellow crystals by adding pyridine to an aqueous solution of ferrous sulphate, has a strong odour of pyridine, is easily decomposed with the formation of basic salts, and, with barium chloride, gives the theoretical quantity of barium sulphate.

Cadmium sulphate tripyridine dihydrate, $CdSO_4,3C_5H_5N,2H_2O$, obtained in a similar manner to the preceding compound, is a white, crystalline precipitate, soluble in water. When heated at 120° for 1 hour, or allowed to remain 35 days exposed to the air, the pyridine is eliminated and $CdSO_4,2H_2O$ remains.

When anhydrous copper sulphate is treated with pyridine, a dark blue, crystalline powder is obtained, which is probably $2CuSO_4,C_5H_5N,H_2O$. It is very unstable, and cannot be obtained in a pure state. It is partially soluble in water with the formation of a basic salt, insoluble in pyridine, and when boiled with absolute alcohol is converted into a green powder. When allowed to remain exposed to the air, it becomes bluish-green, and thus has the composition $2CuSO_4,C_5H_5N,4H_2O$. The *compound*, $2CuSO_4,3C_5H_5N$, obtained by digesting anhydrous copper sulphate with absolute alcohol and excess of pyridine for some time, is a bright blue powder, which, when boiled with absolute alcohol, is converted into the compound $CuSO_4,C_5H_5N$, identical with the pyridine copper sulphate obtained by Jörgensen by heating copper dipyridine sulphate, and by Lang by heating the compound
$$CuSO_4,C_5H_5N,3H_2O$$
at 110°.

Lead chloride pyridine, $PbCl_2,C_5H_5N$, obtained by boiling lead peroxide with a solution of pyridine hydrochloride in hydrochloric acid, crystallises quickly from the filtered solution in beautiful, white crystals.

Manganese tetrachloride dipyridine, $MnCl_4,2C_5H_5N$, is obtained by warming freshly precipitated manganese dioxide with pyridine hydrochloride dissolved in hydrochloric acid. On concentrating the filtrate on the water-bath, it separates in large, bright green crystals, which give a colourless solution with water; when allowed to remain exposed to the air, it loses chlorine and is converted into the compound $MnCl_2,2C_5H_5N$.

Manganous chloride dipyridine, $MnCl_2,2C_5H_5N$, obtained by adding excess of pyridine to a concentrated solution of manganous chloride, separates in brown crystals which darken on exposure, is easily soluble in warm water, and when heated at 160—165° is converted into the compound $MnCl_2,1\frac{1}{2}C_5H_5N$.

Manganous chloride diquinoline, $MnCl_2,2C_9H_7N$, obtained by adding excess of quinoline to an alcoholic solution of manganous chloride, separates in brown crystals, is insoluble in cold water, dissolves in hot water with decomposition, and is soluble in cold alcohol.

Cadmium bromide diquinoline, $CdBr_2,2C_9H_7N$, obtained by boiling cadmium bromide with excess of quinoline, separates from absolute alcohol in white prisms, and is sparingly soluble in cold water.

E. C. R.

Pyridine Compounds of Quadrivalent Palladium.—By ARTHUR ROSENHEIM and THEODOR A. MAASS (*Zeit. anorg. Chem.*, 1898, **18**, 331—338).—Amine bases of quadrivalent palladium have not yet been obtained. The dipalladamine chloride, $Pd_2Cl_2(NH_3Cl)_4$, described by Deville and Debray (*Compt. rend.*, **86**, 926) is a mixture consisting for the most part of ammonium palladium chloride $(NH_4)_2PdCl_6$, and this is the only compound which the authors were able to isolate by the action of chlorine water on palladosamine chloride in the cold. By the action of chlorine water at higher temperatures, ammonium palladious chloride, $(NH_4)_2PdCl_4$, is formed, with evolution of nitrogen. The action of bromine on palladosamine chloride takes place in a similar manner. The pyridine bases of quadrivalent palladium are, however, easily obtained.

Palladodipyridine chloride, $Pd(C_5H_5N)_2Cl_2$, is obtained by adding pyridine to a solution of palladious chloride; a red precipitate is obtained which dissolves when boiled with excess of pyridine, and on adding strong hydrochloric acid, palladodipyridine chloride is precipitated as a bright yellow, crystalline powder.

Palladidipyridine chloride, $Pd(C_5H_5N)_2Cl_4$ obtained by the action of chlorine on the preceding compound suspended in chloroform, crystallises in small, dull, orange prisms, gives off chlorine when exposed to damp air, and is fairly stable in dry air; when heated with potassium hydroxide, a brown precipitate of palladium hydroxide is obtained, and when the cold product is carefully neutralised with hydrochloric acid, potassium palladichloride, K_2PdCl_6, crystallises out in characteristic cherry-red octahedra. When shaken with an

aqueous solution of potassium iodide, two atoms of chlorine are eliminated, and palladodipyridine chloride is formed.

Palladidipyridine dibromochloride, $Pd(C_5H_5NBr_2)_2Br_2Cl_2$, obtained by shaking palladodipyridine chloride suspended in chloroform with bromine, is a deep orange-red, crystalline powder, and is much less stable than the preceding compound. When boiled with potassium hydroxide and then neutralised, potassium palladichloride is obtained. The authors were unable to obtain a similar compound by the action of bromine on palladodipyridine bromide.

Palladidipyridine di-iodochloride, $Pd(C_5H_5N)_2I_2Cl_2$, obtained in a similar manner to the preceding compounds, crystallises in brown needles, and is remarkably stable on exposure to the air. When boiled with water or with potassium hydroxide, it is completely decomposed, with the formation of black palladious iodide. When, however, it is shaken with pure carbon bisulphide, it gives off two atoms of iodine, and is quantitatively converted into palladodipyridine chloride.   E. C. R.

Derivatives of Nicotinic Acid. By AMÉ PICTET and G. SUSSDORFF (*Chem. Centr.*, 1898, i, 677—678 ; from *Arch. Sci. phys. nat. Genève*, [iv], 5, 113—128).—An 82 per cent. yield of nicotinic acid is obtained by pouring a solution of 10 grams of nicotine in 100 c.c. of water and 20 grams of concentrated nitric acid into 250 grams of concentrated nitric acid, and heating the mixture on the water-bath until no more red fumes are evolved ; the *nitrate* of the acid, which is obtained on evaporation, melts at 185°. Nicotinic acid, prepared from the nitrate by means of the copper compound or by heating with acetic anhydride or by distilling alone, crystallises in white needles and melts at 229°. *Ethylic nicotinate*, obtained by treating the acid with alcohol and hydrochloric acid, boils at 220—221° under a pressure of 724 mm.; the nitrate melts at 185°, and the hydrochloride at 126—127°. By the action of fatty amines on ethylic nicotinate, the following amides were prepared. *Methylnicotinamide*, C_5NH_4·CO·NHMe, crystallises from chloroform in long needles and melts at 104—105° ; the *methiodide*, $C_7H_8NO_2$,MeI, crystallises in needles, melts at 174°, and with silver nitrate forms the corresponding nitrate which crystallises from a mixture of alcohol and ether in prisms, and melts at 155—156°. By treating methylnicotinamide methiodide with silver oxide, an aqueous solution of the hydroxide is obtained, which, on evaporation, decomposes into methylamine and trigonellin. *Amylnicotinamide* boils at 191—193° under a pressure of 8 mm., and is easily soluble in ether. *Allylnicotinamide* boils at 186—189° under a pressure of 8 mm., at 315—316° under the ordinary pressure, and cannot be purified by distillation. By preparing the chloride by acting on nicotinic acid with phosphorus pentachloride, removing the phosphorus oxychloride, and then treating the residue with aromatic amines, hydrochlorides of substituted aromatic amides are obtained, and these, with sodium carbonate, yield the free amides. *Nicotinanilide*, C_5NH_4·CO·NHPh, crystallises from water in needles containing $2H_2O$ and melts at 85° ; the anhydrous compound crystallises from a mixture of light petroleum and benzene or light petroleum and chloro-

form in needles and melts at 132°. *Nicotinoparatoluidide* crystallises from water in needles and melts at 150°. Attempts to introduce a methyl group into allylnicotinamide failed, but potassium-methylnicotinamide and allylic iodide yield *methylallylnicotinamide* as a viscous liquid. Attempts to remove water from the latter compound, and to obtain nicotyrine from methylnicotinamide and allylic alcohol at 160—170° also failed.

Piperidine nicotinate, $C_5NH_4 \cdot COOH, C_5NH_{11}$, crystallises in long, colourless needles and melts at 122°. E. W. W.

Transformation of Fatty Ketazines and Aldazines into Pyrazoline Derivatives. By Theodor Curtius and Ed. Zinkeisen *J. pr. Chem.*, 1898, [ii], **58**, 310—332. Compare Abstr., 1894, i, 348).—Maleates of pyrazolines, $NH {<}^{N == CR}_{CRMe \cdot CH_2}$ [R:R:Me = 3 : 5 : 5], are obtained by treating ketazines, $CRMe \colon N \cdot N \colon CRMe$ (Abstr., 1891, 1355), with maleic acid, sometimes in alcoholic solution, and purifying the product by dissolving it in alcohol and precipitating it with ether ; the free base is obtained by treating this product with potash. Only ketazines which contain at least one methyl group, $>C \colon N \cdot N \colon CMe-$, are capable of reacting in this way ; diethylketazine, $CEt_2 \colon N \cdot N \colon CEt_2$, for example, will not do so. The pyrazoline derivatives obtained distil without decomposition under diminished pressure ; the boiling point and index of refraction increase with the molecular weight, whereas the specific gravity decreases. They are stable in the presence of acids, yielding no hydrazine salt, even on boiling, but potassium permanganate oxidises them readily, the molecule being completely broken up. They are not coloured by oxidising agents in dilute solution (Knorr's pyrazoline reaction ; probably only given by derivatives in which the NH-group has become NPh). Of the compounds described, only 5-methylpyrazoline resembles pyrazoline itself (Abstr., 1895, i, 248) in other respects ; the rest do not form azo-dyes, they are not coloured yellow by nitrous acid, they do not colour a pine splint yellow, and they are not oxidised to pyrazoles by bromine.

3 : 5 : 5-Trimethylpyrazoline boils at 57—59° under 14 mm. pressure ; sp. gr. = 0·903 at 18°, 0·907 at 10° ; index of refraction $n_D = 1·46149$ at 10° ; when oxidised with dilute permanganate nitrogen, carbonic anhydride and pyruvic acid are formed ; when treated with bromine in chloroform solution, its own *hydrobromide*, which melts at 171°, is the product. 5-*Methyl*-3 : 5-*diethylpyrazoline* boils at 90—93° under 20 mm., at 78—80° under 14 mm. pressure ; sp. gr. = 0·898 at 18° ; the hydrochloride, platinochloride, picrate, methiodide, and benzoyl derivatives are oils which would not crystallise ; with bromine, an oily product was obtained that was not the hydrobromide ; in the air, this pyrazoline evolves nitrogen, and yields a substance, $C_8H_{14}O$, boiling at 157—158°, which forms an oily compound with phenylhydrazine, and decolorises an ethereal solution of bromine, and so is probably $CEtO \cdot CH \colon CMeEt$, a homologue of mesitylic oxide, although it does not, like the latter, condense with hydrazine ; this substance is also obtained as a bye-product in the preparation of the pyrazoline. 5-*Methyl*-3 : 5-*dipropylpyrazoline* boils at 101—103° under 14 mm., at

113—115° under 20 mm. pressure ; sp. gr. = 0·884 at 18°, 0·888 at 10° ; $n_D = 1·46318$; in other respects, it resembles the previous compound. 5-*Methyl*-3 : 5-*dihexylpyrazoline* is not formed very readily, and was obtained only in small amount.

Ethylideneazine, $CHMe:N\cdot N:CHMe$, can be prepared by shaking an ethereal solution of acetaldehyde with an aqueous solution of hydrazine hydrate, and cooling with water ; it boils at 95—96° under 760 mm. pressure, and has sp. gr. = 0·832 at 17° ; at 180°, it is almost unchanged, but at a higher temperature it gives off nearly all its nitrogen as gas, no butylene being formed, however ; it is fairly stable towards alkalis, but acids decompose it into acetaldehyde and hydrazine. With maleic acid, it yields the *maleate* of 5-*methylpyrazoline*, and this, when decomposed with caustic potash, and the product fractionated, yields a small quantity of the pyrazoline, together with much of a bye-product (see below). The base boils at 73° under 55 mm., at 68° under 45 mm. pressure ; the *benzoyl* derivative melts and decomposes at 156° ; a red *tolueneazo*-derivative, with green reflex, was obtained ; and with bromine in chloroform solution, 5-methylpyrazole appears to be formed. The bye-product mentioned above, $C_{16}H_{26}N_6$, possibly has the constitution

$$C_3N_2H_4Me\cdot CMe{<}{CH\cdot C_3N_2H_4Me \atop CH\cdot C_3N_2H_4Me} ;$$
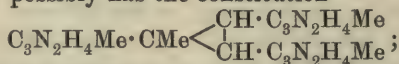
its *hydrochloride* and *picrate* melt and decompose at 148° and 142° respectively ; it takes up 6Br, gives a yellow coloration with nitrous acid, colours wood yellow, and reduces ammoniacal silver solution.

<div align="right">C. F. B.</div>

Stereoisomerism in Piperazine and Ethylenediamine Derivatives. By WILLEM VAN RIJN (*Chem. Centr.*, 1898, i, 727 ; from *Ned. Tijdsch. Pharm.*, **10**, 43—52. See this vol., i, 77).—*Diethylpiperazine*, prepared by warming an aqueous solution of piperazine with an excess of potassium ethylic sulphate, is purified by crystallising the platinochloride from hot dilute hydrochloric acid. By the action of methylic iodide (4 mols.) on piperazine, the *compound* $NHMeI{<}{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}{>}NMe_2I$ is formed ; it crystallises from water in small prisms, decomposes at 260° without melting, and, with cadmium iodide (1 mol.), forms a double salt which crystallises in small, white prisms. The *compound* $NEt{<}{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}{>}NEt_2I$, prepared by the action of ethylic iodide on piperazine, crystallises from alcohol in white needles, melts at 240°, and is insoluble in cold water, ether, chloroform, light petroleum, benzene, and carbon bisulphide ; the cadmium iodide compound crystallises in white needles. The action of propylic iodide on piperazine is analogous to that of ethylic iodide. Attempts to prepare an isomeride of the hydrochloride of dibenzylpiperazine methiodide by the action of freshly precipitated silver chloride on the dibenzylpiperazine methiodide obtained from the hydrochloride by means of sodium hydroxide, resulted only in the production of the original compound. By the action of propylic iodide on methylethylethylenediamine, the mono- and di-propiodides

are formed, and may be separated by means of the platinochlorides. The platinochloride of the former crystallises in reddish needles, and that of the latter in reddish-yellow leaflets. No other salts could be obtained in a crystalline form. E. W. W.

Aromatic Diurethanes of Piperazine. By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1897, **125**, 1182—1184).—Molecular proportions of piperazine and phenylic carbonate, when heated in alcoholic solution for 20 hours, give an almost theoretical yield of the *diurethane*, $COOPh \cdot N : C_4H_8 : N \cdot COOPh$, which forms prismatic crystals and melts at 177—178°; its constitution is established by hydrolysis with potash, and by decomposition with concentrated sulphuric acid.

The a- and β-*naphthylic diurethanes*, prepared in a similar manner, form white, mammelated crystals somewhat insoluble in ordinary solvents; the a-compound melts at 190—191°, the β- at 220°.

The guaiacol *derivative*, $C_4N_2H_8(COO \cdot C_6H_4 \cdot OMe)_2$, crystallises from alcohol in plates and melts at 181°. G. T. M.

Derivatives of Triazole. By JOHANNES THIELE and WILHELM MANCHOT (*Annalen*, 1898, **303**, 33—56. Compare Thiele and Heidenreich, Abstr., 1894, i, 57).—Formamidoguanidine *nitrate*, $COH \cdot NH \cdot NH \cdot C(:NH) \cdot NH_2, HNO_3$, prepared by heating amidoguanidine nitrate with 90 per cent. formic acid and one drop of nitric acid on the water-bath, crystallises from water and melts at 143°; the *picrate* crystallises in needles and melts at 193°. *Oxalylamidoguanidine*, $COOH \cdot CO \cdot NH \cdot NH \cdot C(NH) \cdot NH_2$, obtained on adding amidoguanidine hydrogen carbonate to a concentrated aqueous solution of oxalic acid, and boiling the liquid in a reflux apparatus, crystallises from water, and melts and evolves gas at 231—232°.

Ammonia is readily eliminated from amidomethyltriazole under the influence of dilute sulphuric acid at 180—190°, the other products being carbonic anhydride, hydrazine, and acetic acid; a 30 per cent. solution of caustic potash or soda, however, leaves the amido-compound for the greater part unchanged. The *benzoyl* derivative of amidomethyltriazole melts and decomposes at 285—290°; the *acetyl* derivative crystallises from water, and remains unfused at 270°.

Methyltriazoleazodimethylaniline, $NMe_2 \cdot C_6H_4 \cdot N_2 \cdot C \underset{N——CMe}{\overset{NH \cdot N}{\lessgtr}}$, prepared by adding dimethylaniline hydrochloride to a solution of diazotised amidomethyltriazole, crystallises from alcohol, and melts and decomposes at 238°; reduction with stannous chloride and hydrochloric acid destroys the colour, which is redeveloped under the influence of ferric chloride.

Methyltriazoleazo-β-naphthylamine, $NH_2 \cdot C_{10}H_6 \cdot N_2 \cdot C \underset{N——CMe}{\overset{NH \cdot N}{\lessgtr}}$, is a red powder, with green, metallic reflex, and melts and decomposes at 270°. The colour is destroyed by reducing agents, and is not redeveloped by ferric chloride.

Chloromethyltriazole, $CCl \underset{N——CMe}{\overset{HN \cdot N}{\lessgtr}}$, obtained by diazotising amidomethyltriazole in concentrated hydrochloric acid, and evaporating the

liquid at the ordinary temperature, melts at 147°; it is volatile in steam, and sublimes when heated on the water-bath. The *silver* derivative is sparingly soluble in water, but readily in ammonia and nitric acid.

Benzylidenemethyltriazylhydrazine, $CHPh{:}N{\cdot}NH{\cdot}C\underset{N-CMe}{\overset{NH{\cdot}N}{\lessgtr}}$, prepared by reducing diazotised amidomethyltriazole, under special precautions, and combining the product with benzaldehyde, crystallises from alcohol and melts at 263°; the *hydrochloride* separates from alcohol in needles, and melts at 256°.

Amidotriazole, $NH_2{\cdot}C\underset{N-CH}{\overset{NH{\cdot}N}{\lessgtr}}$, obtained on heating aqueous formamidoguanidine nitrate with sodium carbonate, crystallises from ethylic acetate and melts at 159°; it closely resembles amidomethyltriazole, but differs from the latter, which is feebly alkaline and has no reducing action, whereas amidotriazole is neutral, and slightly reduces a boiling, ammoniacal solution of silver nitrate. The *nitrate* melts and decomposes at 174°, and the *picrate*, which crystallises in yellow needles, melts and decomposes at 227—228°. *Azotriazole*, $N_2(C_2H_2N_3)_2$, prepared by oxidising amidotriazole with potassium permanganate in alkaline solution, dissolves in alkalis, and is precipitated by acids. Hydrazotriazole *hydrochloride*, which is formed when azotriazole is reduced with stannous chloride and hydrochloric acid, crystallises in white needles and melts at 227—230°, beginning to decompose before this temperature is reached. It reduces ferric chloride and ammoniacal silver nitrate, and aqueous solutions readily undergo oxidation when exposed to the air. *Triazoleazodimethylaniline*, produced on adding dimethylaniline hydrochloride to a solution of diazotised amidotriazole, crystallises from alcohol, and melts and decomposes at 250°.

Chlorotriazole, $CCl\underset{N-CH}{\overset{NH{\cdot}N}{\lessgtr}}$, prepared by diazotising amidotriazole in concentrated hydrochloric acid, crystallises from benzene in slender needles, and melts at 167°; it sublimes when heated, and is volatile in vapour of benzene. It yields salts with acids, and also forms metallic derivatives.

Amidotriazolecarboxylic acid, $NH_2{\cdot}C\underset{N-C{\cdot}COOH}{\overset{NH{\cdot}N}{\lessgtr}}$, obtained by heating oxalylamidoguanidine (2 mols.) with sodium carbonate on the water-bath, melts at 182° with elimination of carbonic anhydride and production of amidotriazole; it dissolves readily in alkalis, and is precipitated by acids. The *picrate* melts at 176°, and the *hydrochloride* melts and decomposes at 171—172°; the *sodium* salt is anhydrous, and the *ethylic* salt crystallises from alcohol and melts at 247°.

Diazotriazolecarboxylic acid, $C_3HN_5O_2 + H_2O$, prepared by diazotising amidotriazolecarboxylic acid, decomposes at 96°; it does not explode when touched with a hot wire, and detonates with difficulty when struck. Chlorotriazole is produced on heating the substance with hydrochloric acid, and triazole results from boiling an alcoholic solution in a reflux apparatus; triazole obtained in this manner melts

at 120—120·5°, and is identical with the compound described by Bladin and by Andreocci. M. O. F.

Hydrazine Derivatives of Propionic Acid. By JOHANNES THIELE and JAMES BAILEY (*Annalen*, 1898, **303**, 75—91. Compare Thiele and Heuser, Abstr., 1896, i, 340).—The *semicarbazone* of acetaldehyde crystallises from alcohol in white needles, and melts at 162°. *Carbonamidohydrazopropionitrile*, $NH_2 \cdot CO \cdot CH \cdot NH \cdot CMe \cdot CN$, prepared by the action of 60 per cent. hydrocyanic acid on the semicarbazone of acetaldehyde, crystallises from alcohol and melts at 131°; it has a powerful reducing action, and yields hydrogen cyanide when heated. *Carbonamidohydrazopropionamide* is obtained by the action of cold concentrated hydrochloric acid on the nitrile for 24 hours; it separates from water in lustrous crystals containing $1H_2O$, and melts at 99—106°, or at 142° in the anhydrous condition.

Dihydroxymethyldihydrotriazine, $OH \cdot C \underset{NH--NH}{\overset{N \cdot C(OH)}{<\!\!\!>}} CMe$, prepared by treating the foregoing nitrile with fuming hydrochloric acid during 48 hours, diluting the liquid with twice its volume of water, and boiling the product for 3 hours in a reflux apparatus, crystallises from alcohol in lustrous scales and melts at 214°. *Dihydroxymethyltriazine*, $OH \cdot C \underset{N===N}{\overset{N \cdot C(OH)}{<\!\!\!>}} CMe$, is obtained by oxidising the dihydro-derivative with bromine water; it softens at 206° and melts at 209°.

The imido-ether of carbonamidohydrazopropionic acid is obtained in the form of the *hydrochloride*,

$$NH_2 \cdot CO \cdot NH \cdot NH \cdot CHMe \cdot C(OEt) \colon NH, 2HCl,$$

when an alcoholic solution of the nitrile is saturated with dried hydrogen chloride; it is very hygroscopic, deliquescing rapidly on exposure to the air, and melts at 124—128°, when it decomposes vigorously. On dissolving the hydrochloride in water, neutralising one-half of the hydrochloric acid with sodium carbonate, evaporating to dryness, and extracting with ethylic acetate, *ethylic carbonamidohydrazopropionate*, $NH_2 \cdot CO \cdot NH \cdot NH \cdot CHMe \cdot COOEt$, is produced; it melts at 108°. The free *acid*, obtained by hydrolysis with baryta, melts and decomposes at 166—168°. Hydrazidopropionic acid, $NH_2 \cdot NH \cdot CHMe \cdot COOH$, prepared by the action of boiling 80 per cent. sulphuric acid on ethylic carbonamidohydrazopropionate, is identical with the compound described by W. Traube and Longinescu (Abstr., 1896, i, 340).

The *semicarbazone* of pyruvonitrile, $NH_2 \cdot CO \cdot NH \cdot N \colon CMe \cdot CN$, obtained by oxidising carbonamidohydrazopropionitrile with potassium permanganate, is a sparingly soluble crystalline powder, which melts and decomposes at 215°; the *semicarbazone* of pyruvamide and the semicarbazone of ethylic pyruvate melt and decompose at 230° and 206° respectively.

Ethylic hydrazopropionate, $N_2H_2(CHMe \cdot COOEt)_2$, prepared, under specified conditions, from hydrazine, aldehyde-ammonia, and hydrogen cyanide, by hydrolysing an alcoholic solution of the product with hydrogen chloride, crystallises from benzene, petroleum, or water in thin, elongated prisms; it melts at 78°, and boils at 245°

under a pressure of 750 mm. The salt can also be obtained from hydrazidopropionic acid, aldehyde-ammonia, and hydrogen cyanide. The *methylic* salt melts at 93°, and boils at 220° under a pressure of 720 mm. The free *acid*, which crystallises from concentrated aqueous solutions in microscopic needles, begins to darken at 180°, and melts and evolves gas at 198°.   M. O. F.

Characteristic Oxidation Reaction of some Cyclic Amines. By EUGEN BAMBERGER and ANTON VON GOLDBERGER (*Ber.*, 1898, **31**, 2636—2640).—The authors have found that the hitherto unknown izimidindazole, $C_6H_4\diagdown\diagup^{C(NH_2)}_{N}\diagup\diagdown NH$, may be oxidised in various ways, but in most cases the product is Weddige and Fluger's hydroxy-β-phenotriazine, the so-called benzazimide, $C_6H_4\diagdown\diagup^{C(OH)\cdot N}_{N}\diagup\diagdown N$

A similar change of structure occurs also when the monomethyl, and dimethyl-izimidindazoles are oxidised; these yield the corresponding monomethyl- and dimethyl-hydroxy-β-phenotriazines.

Hydroxy-β-phenotriazine partakes of the nature of a diazoamido-compound, as its formula indicates. It gives a brilliant red colour with β-naphthylamine, and with melted resorcinol it yields a colouring matter, *benzamidoazoresorcinol*, which crystallises in rosettes of dark-red needles. Its structure is probably $NH_2 \cdot CO \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH)_2$.

When izimidindazole is oxidised in alkaline solution by means of a ferricyanide or even by air, a basic *substance* is formed, which has colouring properties and forms crystals having an intense green metallic sheen; it gives a sparingly soluble nitrate, and may be diazotised.   A. L.

Azo- and Hydrazo-compounds of Tetrazole. By JOHANNES THIELE (*Annalen*, 1898, **203**, 57—75. Compare Abstr., 1894, i, 61), When amidotetrazole is oxidised by potassium permanganate in feebly alkaline solution, it is completely decomposed, but in presence of much alkali, derivatives of azotetrazole are produced. The *sodium*, *potassium*, and *barium* derivatives contain $5H_2O$, and the *calcium* derivative $8H_2O$, the *ammonium* derivative is anhydrous, and crystallises from water in yellow needles, which decrepitate at 210° without exploding. The *hydroxylamine* derivative contains $2H_2O$, and explodes violently at high temperatures; the *hydrazine* derivative also contains $2H_2O$, and the *amidoguanidine* derivative crystallises in long, yellow needles containing $1H_2O$. The *diazoguanidine* derivative, $C_4H_8N_{20}$, is anhydrous.

When an aqueous solution of azotetrazole is treated with excess of a mineral acid, tetrazylhydrazine is produced, with elimination of nitrogen and formic acid; oxalic acid gives rise to diazoimide. On adding dilute acid to an aqueous solution of sodium azotetrazole covered with ether, the latter takes up a considerable amount of azotetrazole; the yellow solution rapidly becomes turbid, however, from separation of a brick-red substance of unknown composition, but which probably contains one tetrazole ring.

Hydrazotetrazole, prepared by boiling an aqueous solution of sodium azotetrazole with magnesium powder, is a white, amorphous compound, insoluble in organic media, and dissolving with great difficulty in boiling water; the substance is precipitated by ammonia and alkalis from the solution in concentrated hydrochloric acid, and the aqueous solution yields precipitates with many metallic salts.

Dibromoformaltetrazylhydrazone, $CBr_2:N\cdot NH\cdot CN_4H$, obtained by the action of bromine water on a solution of hydrazotetrazole in concentrated hydrobromic acid, crystallises from ether in white needles containing $\frac{1}{2}H_2O$; it becomes brown when heated, and melts at 177°. Concentrated sulphuric acid eliminates hydrogen bromide and carbonic anhydride, forming tetrazylhydrazine. Further treatment of hydrazotetrazole with bromine converts it into isocyanogen tetrabromide (*loc. cit.*).

Methylic azinocarbonate, $N_2[:C(OMe)_2]_2$, prepared by the action of potash dissolved in methylic alcohol on isocyanogen tetrabromide, separates from ethylic acetate in beautiful crystals, and melts at 111°; dilute acids resolve the substance into methylic carbonate and hydrazine.

The *sodium* derivative of the amide of tetrazoleazocarboxylic acid, obtained by oxidising an alkaline solution of tetrazylsemicarbazide (Abstr., 1896, i, 107) with potassium permanganate, crystallises from water in lustrous, orange plates containing $2H_2O$; caustic potash eliminates ammonia, and gives rise to the *potassium* salt of tetrazolecarboxylic acid, which is decomposed by dilute acids, yielding carbonic anhydride, formic acid, nitrogen, and hydrazine, not tetrazole. Tetrazoleazodimethylaniline is decomposed by dilute acids in the same way. M. O. F.

Derivatives of Amido-orcinol. By FERDINAND HENRICH (*Monatsh.*, 1898, **19**, 483—517. Compare Abstr., 1897, i, 446).— *Tribenzoylamido-orcinol*, $NHBz\cdot C_6H_2Me(OBz)_2$, formed when amido-orcinol is shaken with an excess of benzoic chloride and soda, crystallises from absolute alcohol in white, prismatic needles, melts at 165—166° (uncorr.), dissolves readily in benzene, chloroform, and hot alcohol, fairly readily in cold alcohol, and sparingly in ether; it yields 3-hydroxy-2'-phenyl-1-methylbenzoxazole when distilled and hydrolysed.

3-Hydroxy-2'-phenyl-1-methylbenzoxazole has a normal molecular weight in boiling acetone, is not altered by boiling with strong hydrochloric acid, but is hydrolysed when heated with it, under pressure, at 183° for 5 hours, yielding benzoic acid and amido-orcinol.

3-Hydroxy-2'-phenylbenzoxazole, $\begin{matrix} CH:CH\cdot C\cdot N \\ OH\cdot C : CH \cdot C\cdot O \end{matrix}\Big\rangle CPh$, is made by treating amidoresorcinol with benzoic chloride, heating the product for 15 minutes at its boiling point, and finally hydrolysing with alcoholic potash the benzoyl derivative thus obtained; it crystallises from benzene in colourless, compact crystals, melts at 216—217°, dissolves readily in acetone, acetic acid, hot alcohol, and ether, but sparingly in light petroleum, cold chloroform, and benzene. Its alkaline solution is reddish-yellow and has a lilac fluorescence.

When 3-hydroxy-2'-phenyl-1-methylbenzoxazole is treated with strong nitric acid, the 2:4-*dinitro*-compound, $C_{14}H_9O_2N(NO_2)_2$, is formed. This separates from alcohol and chloroform in yellow, rhombohedral

crystals and melts at 188—189°, is sparingly soluble in cold alcohol, ether, acetic acid, and petroleum, but dissolves somewhat more readily in hot benzene and chloroform ; it has very feeble tinctorial properties, decomposes carbonates, liberating carbonic anhydride, and gives a crystalline *sodium* salt.

3-Hydroxy-2′-phenyl-1-methylbenzoxazole is not affected by nitrous acid, but reacts in alkaline solution with diazobenzene, yielding *benzeneazo-3-hydroxy-2′-phenyl-1-methylbenzoxazole*, $C_{20}H_{15}N_3O_2$, which crystallises from glacial acetic acid in brownish-yellow needles and melts at 169—170°, dissolves readily in benzene and chloroform, but sparingly in cold alcohol and ether ; sulphuric acid dissolves it, forming a yellowish-red solution which becomes redder on dilution. The *hydrochloride*, $C_{20}H_{15}N_3O_2,HCl$ (?), separates on passing hydrogen chloride into an ethereal solution of the base ; it decomposes very quickly in presence of moisture.

Acetoxybenzeneazo-3-hydroxy-2′-phenyl-1-methylbenzoxazole,
$$C_{20}H_{14}N_3O_2Ac,$$
made by heating the foregoing base with acetic chloride and anhydrous sodium acetate, crystallises from alcohol in long, orange-coloured, apiculate prisms and melts at 182—183° ; it is only slowly hydrolysed by boiling aqueous or alcoholic alkalis. The corresponding *hydrazo*-compound, made by heating it with zinc dust and acetic acid, crystallises from acetic acid in long leaflets and melts at 184—185° ; it dissolves in strong sulphuric acid, giving a faintly coloured solution having a steel-blue fluorescence ; on oxidation with nitrous acid, it yields the original hydroxyphenylmethylbenzoxazole. The corresponding *benzoyl* derivative, $C_{20}H_{14}N_3O_2Bz$, crystallises from absolute alcohol in light, brownish-yellow, prismatic, pointed crystals, sinters at 160°, and melts at 171° ; it resembles the corresponding acetyl compound in its behaviour towards concentrated sulphuric acid and alkalis. On reduction, it yields a *compound* which dissolves in alkalis and in sulphuric acid, and the solution in the latter instance has a steel-blue fluorescence ; it gives hydroxyphenylmethylbenzoxazole on treatment with nitrous acid.

Paramethoxybenzeneazo-3-phenyl-1-methylbenzoxazole, $C_{20}H_{24}N_3O \cdot OMe$, produced when the azo-compound is treated with sodium methoxide and methylic iodide, crystallises from absolute alcohol in small, yellow needles, sinters at about 135°, and melts at 149—150° ; it dissolves readily in cold benzene, chloroform, ethylic acetate, ether, and hot alcohol, but only sparingly in light petroleum and cold alcohol.

3-*Hydroxy*-1 : 2′-*dimethylbenzoxazole*, $\begin{matrix} CH : CMe \cdot C \cdot N \\ | \quad\quad || \\ C(OH):CH \cdot C \cdot O \end{matrix} \!\!> CMe$, formed when triacetylamido-orcinol is hydrolysed with diluted sulphuric acid or concentrated hydrochloric acid, crystallises from alcohol or benzene in long, colourless needles, melts at 210°, and dissolves readily in acetic acid, warm ether, and alcohol, but only sparingly in benzene and light petroleum. Its *acetyl* derivative, $C_{11}H_{11}O_3N$, formed by heating triacetylamido-orcinol at its boiling point for some time, crystallises from petroleum in white needles, melts at 65°, and is readily soluble in the ordinary media ; it yields the preceding compound on hydrolysis with alcoholic potash. The *benzoyl* derivative, $C_9H_8O_2N \cdot COPh$,

crystallises from petroleum, melts at 108—110°, and dissolves readily in the usual solvents, with the exception of light petroleum.

Benzeneazo-3-hydroxy-1 : 2′-dimethylbenzoxazole, made by the action of diazobenzene in alkaline solution on hydroxydimethylbenzoxazole, melts at 116—118°, and dissolves readily in the usual media; it behaves towards strong sulphuric acid like the corresponding derivative of phenylmethylbenzoxazole, but is much more readily soluble in soda.

Formamido-orcinol, $C_7H_5(OH)_2 \cdot NH \cdot CHO$, obtained when sodium formate and anhydrous formic acid are heated with amido-orcinol hydrochloride at the temperature of a glycerol bath, sinters at 180°, melts and becomes red at 195—198°, and dissolves readily in alcohol and hot water, somewhat sparingly in ether, benzene, and chloroform, and is insoluble in light petroleum. It is quickly dissolved by aqueous soda, and reduces Fehling's solution and ammoniacal silver nitrate.

3-Hydroxy-1-methylbenzoxazole, $OH \cdot C_7H_5 <^N_O> CH$, produced when the formyl compound is heated at 208°, forms long, colourless leaflets and melts at 162—163° after sintering slightly; it is readily soluble in acetic acid, alcohol, and ether, somewhat readily in benzene, and sparingly in chloroform and light petroleum, especially in the cold; it dissolves in strong soda ley, forming a colourless solution, but is not dissolved by a dilute solution of soda; it yields amido-orcinol when hydrolysed by strong hydrochloric acid.

3-Benzoxy-1-methylbenzoxazole, $C_8H_6NO_2Bz$, is readily soluble in alcohol, ether, benzene, acetic acid, carbon bisulphide, and chloroform, but only sparingly in cold petroleum. It is insoluble in alkalis, melting to an oil when warmed with them. *Benzeneazo-3-hydroxy-1-methylbenzoxazole*, $C_{14}H_{11}N_3O_2$, forms elongated leaflets having an intense purple colour, and melts at 186°; it dissolves readily in benzene and chloroform, but only sparingly in petroleum and in cold alcohol or acetone; it forms a yellowish solution in strong sulphuric acid, which becomes a deeper red on dilution, and dissolves more readily in aqueous soda than do the corresponding 2′-phenyl- and 2′-methyl-derivatives. A. L.

New Synthesis of Paraxanthine.—By EMIL FISCHER and HANS CLEMM (*Ber.*, 1898, **31**, 2622—2623).—*Chloroparaxanthine*, $NMe \cdot CO \cdot C \cdot NMe$ / $CO \cdot NH \cdot C —N > CCl$, is formed when 1 : 7-dimethyluric acid is heated with phosphorus oxychloride at 135—140° for 3 hours, and can be purified by boiling with alcohol and subsequent recrystallisation from a large bulk of hot water; it melts at 284° (295° corr.), dissolves in 170 parts of hot water, and crystallises from it on cooling in colourless, interlacing prisms; it is more readily soluble in hot alcohol. When heated, it melts and sublimes readily, slight decomposition occurring. The *sodium* salt is sparingly soluble in cold water, and separates from hot water in slender, shining needles; the *potassium* salt is more readily soluble, and crystallises in spherical aggregates of slender, colourless needles. Chloroparaxanthine dissolves readily in cold dilute ammonia, and the solution gives, with silver nitrate, a white, amorphous precipitate which blackens when

warmed, and dissolves in warm dilute nitric acid, the solution depositing slender needles on cooling.

Chloroparaxanthine is readily reduced to paraxanthine when warmed with hydriodic acid and phosphonium iodide.   A. L.

Xanthine Bases from Uric Acid. By Ernst E. Sundvik (*Zeit. physiol. Chem.*, 1898, **26**, 131—132).—In a previous paper (Abstr., 1897, i, 598), it is stated that, by reduction of uric acid, xanthine and hypoxanthine are probably formed. This view is now shown to be correct, the bases having been isolated and analysed.   W. D. H.

Some Properties of Caffeine. By E. Tassilly (*Bull. Soc. Chim.*, 1897, [iii], **17**, 596—599).—Hydrated caffeine, $C_8H_{10}N_4O_2 + H_2O$, does not lose all its water of crystallisation even at 150°, at which temperature it is partially volatile. At 110°, the anhydrous compound does not lose in weight, whereas the hydrate undergoes a loss of 6·93 per cent. Caffeine is not volatile with steam. Calcium hydroxide solution decomposes the alkaloid at 100°, ammonia being evolved, whilst with magnesia under similar circumstances no trace of ammonia is given off. The partition of caffeine between different solvents ceases to be normal when other extractive substances are present.   J. J. S.

Hydurinephosphoric Acid. By Emil Fischer (*Ber.*, 1898, **31**, 2547—2549).—Finely-powdered trichloropurine, $C_5HN_4Cl_3$, is added to 10 times its weight of hydriodic acid (sp. gr. 1·96), excess of powdered phosphonium iodide added, and the mixture kept, first for an hour at 0° with frequent shaking, and then shaken at the ordinary temperature for 24 hours by means of a motor; the product is then warmed to 40°, filtered, evaporated at 40—50° under diminished pressure, mixed with a little water, and again evaporated; the crystalline residue is washed with a little cold water and recrystallised from dilute hydriodic acid, warming gently only. In this way, the *hydriodide* of hydurinephosphoric acid, $C_4H_9N_4PO_3,HI + H_2O$, is obtained; by treatment with water and freshly precipitated silver iodide, it can be converted into the *hydrochloride*, $C_4H_9N_4PO_3,HCl$. These salts are soluble in water, but the solution soon turns red; this coloration is hindered by the presence of a little halogen acid, but promoted by alkalis, the colour when ammonia is present becoming eventually that of a potassium permanganate solution. When heated with dilute hydrochloric acid on the water-bath, the hydrochloride yields ammonium chloride and phosphoric acid, but no phosphorous acid. The base corresponding with these salts is *hydurinephosphoric acid*, which is probably $C_4H_7N_4 \cdot PO(OH)_2$, derived from a hypothetical base hydurine, $C_4H_8N_4$, in the same way as is the amidophosphoric acid, $NH_2 \cdot PO(OH)_2$, from ammonia, NH_3.   C. F. B.

Purine and its Methyl Derivatives. By Emil Fischer (*Ber.*, 1898, **31**, 2550—2574).—2-*Iodo-7-methylpurine*, $\begin{array}{c} N{:}CH \cdot C \cdot NMe \\ CI{:}N \cdot C{-}{-}N \end{array}{>}CH$,

is obtained by reducing 2 : 6-dichloro-7-methylpurine (Abstr., 1898, i, 97) with hydriodic acid in large excess and phosphonium iodide at 0°;

it melts at 229° (corr.). When boiled with normal potash, it is converted into 2-*oxy*-7-*methylpurine*, $\begin{array}{c}\text{N:CH---C·NMe}\\ \text{CO·NH·C---N}\end{array}\!\!\!\!>\!\!\text{CH} + H_2O$, which decomposes at about 323°, and with normal potassium hydrosulphide solution in large excess, into an analogous, yellow *thio*-compound which decomposes at about 295°. With half-saturated alcoholic ammonia at 145—150°, it yields 2-*amido*-7-*methylpurine*,

$$\begin{array}{c}\text{N : CH · C·NMe}\\ \text{NH}_2\text{· C}\!=\!\text{N}\!-\!\text{C}\!-\!\text{N}\end{array}\!\!\!\!>\!\!\text{CH},$$
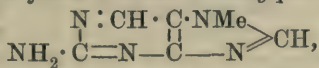
melting at 283° (corr.), which can also be obtained from 2-chloro-7-methylpurine (see below), a compound that is more easily prepared than 2-iodo-7-methylpurine. When boiled with zinc dust and water, it yields 7-*methylpurine*, $\begin{array}{c}\text{N:CH·C·NMe}\\ \text{CH:N·C---N}\end{array}\!\!\!\!>\!\!\text{CH}$; this melts at 184° (corr.), its *mercurichloride* at 252°(corr.), and its *methiodide* at 231—232° (corr.).

2-*Chloro*-7-*methylpurine*, $\begin{array}{c}\text{N:CH·C·NMe}\\ \text{CCl:N·C---N}\end{array}\!\!\!\!>\!\!\text{CH}$, obtained by boiling 2 : 6-dichloro-7-methylpurine or trichloro-7-methylpurine with zinc dust and water, melts at 200—201° (corr.), the *mercurichloride* at 206—207°. When it is boiled wlth normal potash solution, a compound, $C_5H_7N_4Cl$, which melts and decomposes at about 251°, is deposited, whilst 2-oxy-7-methylpurine remains dissolved in the alkali.

2 : 6-*Di-iodopurine*, $\begin{array}{c}\text{N:CI·C·NH}\\ \text{CI:N·C---N}\end{array}\!\!\!\!>\!\!\text{CH}$, obtained by heating trichloropurine (Abstr., 1898, i, 47) with hydriodic acid and phosphonium iodide, melts and decomposes at about 224°; when heated with hydrochloric acid (sp. gr. = 1·19) at 100° in a sealed tube, it yields xanthine, and when boiled with zinc dust and water, the insoluble zinc salt of purine itself is formed, and remains mixed with the excess of zinc dust. *Purine*, $\begin{array}{c}\text{N:CH·C·NH}\\ \text{CH:N·C---N}\end{array}\!\!\!\!>\!\!\text{CH}$, is a readily soluble, well crystallised substance, which forms salts both with acids and with bases, and as regards its character in general falls naturally in the series uric acid, xanthine, hypoxanthine, purine. It melts at 216—217° (corr.); the *nitrate*, with $1HNO_3$, melts and decomposes at about 205°; the yellow *picrate*, with $1C_6H_3N_3O_7$, melts at about 208°; the base is very stable towards oxidising agents, and in consequence does not give the murexide reaction.

2(?)-*Chloro*-9-*methylpurine*, prepared by boiling trichloro-9-methylpurine (see below) with zinc dust and water, melts at 135—136° (corr.). When heated with half-saturated alcoholic ammonia at 150°, it is converted into 2(?)-*amino*-9-*methylpurine*, which melts at 247° (corr.); with hydriodic acid (sp. gr. = 1·96) at the ordinary temperature, it yields 2(?)-*iodo*-9-*methylpurine* melting at 171—172° (corr.). This, when boiled with zinc dust and water, yields 9-*methylpurine*, $\begin{array}{c}\text{N:CH·C---N}\\ \text{C H:N·C·NMe}\end{array}\!\!\!\!>\!\!\text{CH}$, which melts at 162—163° (corr.).

Preparation of Trichloro-9-*methylpurine.*—This is best prepared with-

out the use of phosphoric chloride ; 2 : 6-dichloro-8-oxy-9-methylpurine (1 part) is heated with phosphorus oxychloride (25 parts) for 10 hours at 160—165°, the product is evaporated under diminished pressure, and the residue washed with cold water and then with cold dilute caustic soda, and recrystallised from alcohol.

Identification of Xanthine.—This is best effected by heating the supposed xanthine (1 part) with bromine (5 parts) at 100° in a sealed tube, opening the tube and heating it to 140—145° to expel bromine, washing the residue with sulphurous acid, dissolving it in warm ammonia and precipitating with hot, dilute sulphuric acid. The bromo-xanthine formed (1 part) is dissolved in normal caustic potash (13 parts by vol.), and heated with methylic iodide ($2\frac{1}{4}$ parts) in a sealed tube at 80° with constant shaking for 2 hours ; the bromocaffeine which separates is washed with very dilute caustic soda and recrystallised from water ; it melts at 206°. This (1 part) is boiled for 5 minutes with 10 per cent. alcoholic potash (7 parts), the mixture is diluted with 3 times its volume of water, and the ethoxycaffeine, which soon separates, is recrystallised from water ; it melts at 140°. By boiling it (1 part) with 10 per cent. hydrochloric acid (10 parts by vol.) it can be converted into hydroxycaffeine, which melts at 345°. All these processes can be carried out with 0·5 gram of xanthine, and in the space of 24 hours.   C. F. B.

Behaviour of 2-Amido-6 : 8-dioxypurine towards Chlorides of Phosphorus. By EMIL FISCHER (*Ber.*, 1898, **31**, 2619—2621).—

6-*Chloro-2-amido-8-oxypurine*, $\mathrm{NH_2 \cdot C}{=}\mathrm{N-C \cdot NH}\!\!\begin{array}{c}\mathrm{N{:}CCl \cdot C \cdot NH}\\ \end{array}\!\!{>}\mathrm{CO}$, made by boil-

ing 2-amido-6 : 8-dioxypurine with phosphorus pentachloride dissolved in phosphorus oxychloride, can be purified by dissolving it in warm dilute ammonia and treating with animal charcoal ; the filtered liquid, heated to drive off ammonia, deposits the substance in bundles of slender, microscopic needles. It decomposes at a high temperature without melting, dissolves sparingly in hot water and still more sparingly in alcohol, is readily soluble in warm dilute mineral acids, and fairly readily in dilute ammonia. When heated at 130° with hydrochloric acid, it yields the hydrochloride of 2-amido-dioxypurine.

When 6-*iodo-2-amido-8-oxypurine*, $C_5H_4N_5OI$, obtained when chlor-amido-oxypurine is heated with fuming hydriodic acid and phosphonium iodide at 100°, it is converted into a colourless, granular, indistinctly crystalline powder, which resembles in properties the original chloro-compound, but is more sparingly soluble.   A. L.

Bases Isomeric with Cinchonine. By VICTOR CORDIER VON LOWENHAUPT (*Monatsh.*, 1898, **19**, 461—482).—When cinchonine hydrobromide is heated with alcoholic potash, a mixture of bases is obtained which may be separated, by means of ether, into two portions. The least soluble portion may be further resolved by crystal-lisation from alcohol, and on treatment with sulphuric acid gives a salt, $(C_{19}H_{22}N_2O)_2,H_2SO_4 + 2H_2O$, which has the same crystalline form as Hesse's homocinchonine sulphate (Abstr., 1881, 615) and melts at 199·5°, and also the sulphate of a new base, *tautocinchonine*. This

base resembles homocinchonine in some respects; it dissolves in 144 parts of absolute alcohol at 20°, melts at 252·5°, and has $[a]_D = + 209\cdot42°$; its *dihydriodide*, $C_{19}H_{22}N_2O,2HI$, forms beautiful, yellow prisms and melts at 238°.

If that portion of the product of hydrolysis of cinchonine hydrobromide which is readily soluble in ether is treated with hydrochloric acid and potassium iodide, it yields *a-isocinchonine dihydriodide*, which forms beautiful, yellow, prismatic crystals, and melts at 205—206°, whilst the mother liquor from which it has been deposited contains a mixture of bases, and by successive treatment with hydrochloric acid and zinc chloride may be made to yield δ-cinchonine hydrochloride and the zincochloride of a new base, *ε-cinchonine*.

When cinchonine hydrobromide is hydrolysed with alcoholic silver nitrate, a mixture of bases is obtained which appear to be identical with those produced when alcoholic potash is employed, and only differ in their relative proportions.

ε-Cinchonine, $C_{19}H_{22}N_2O$, melts at 152°, dissolves very readily in alcohol, but more sparingly in ether; it crystallises from the latter in long, slender needles, and its specific rotation in 1 per cent. alcoholic solution at 20° $[a]_D = 66\cdot99$. Its *hydrochloride*, $C_{19}H_{22}N_2O,HCl$, is anhydrous and crystallises in thick prisms.

When water is used to hydrolyse cinchonine hydrobromide, a product is obtained from which ether dissolves δ-cinchonine and a-isocinchonine, leaving pseudocinchonine and what is probably apoisocinchonine (allocinchonine ?).

When hydrobromic acid acts on cinchonine, not only is cinchonine hydrobromide formed, but the hydrobromides of a-isocinchonine, pseudocinchonine, and δ-cinchonine are also produced.　　　A. L.

Cinchonicine. By FERDINAND ROQUES (*Ann. Chim. Phys.*, 1897, [vii], 10, 234—288).—The production of crystallised cinchonicine has already been described (Abstr., 1895, i, 688). Full details of the method employed are set forth in the paper; the specific rotation of the base obtained either from cinchonine or cinchonidine is now given as $[a]_D = 57\cdot60°$; it was formerly stated to be 48·25°. The base from either of the two alkaloids melts at 49—50°, differing in this respect from von Miller and Rhode's cinchotoxine, which melts at 58—59°; the two bases are otherwise very similar, and they may be identical (compare Abstr., 1895, i, 434).

The *basic nitrate* crystallises readily in prisms, which melt and decompose at 160°; $[a]_D = 29\cdot58°$, the *normal nitrate* in yellow, silky needles, extremely soluble in water; its alcoholic solution is yellow, the colour disappearing when half the acid is neutralised by potash. The *normal succinate*, $C_{19}H_{22}N_2O,C_4H_6O_4 + H_2O$, crystallises in prisms.

The double zinc and cadmium chlorides, and the alkylic haloid salts have already been described (Abstr., 1895, i, 688).　　　G. T. M.

Chemistry of the Atropine Alkaloids. By ADOLF PINNER (*Chem. Centr.*, 1898, i, 679; from *Centr. prakt. Augenheilk.*, 20, 1—9). —According to the author, the plants of the order of *Solanaceæ*, and the

species *Atropa*, *Hyoscyamus*, *Datura*, *Mandragora*, *Solanum*, and *Anisodus* contain at least the two alkaloids, hyoscyamine, $C_{17}H_{23}NO_3$, and hyoscine (scopolamine). The former, by the action of alkalis, yields atropine, which may, perhaps, occur in small quantities in the plants, whilst hyoscine, with alkalis, forms inactive scopolamine (atroscine). By the loss of water, hyoscyamine and atropine form apoatropine, which, by an intramolecular change, yields belladonnine. Atropine is always present in commercial hyoscyamine and inactive hyoscine (atroscine), hyoscyamine and atropine are contained in commercial scopolamine, whilst duboisine contains hyoscyamine, hyoscine, and other alkaloids. All the alkaloids, when hydrolysed, yield tropic acid ; $C_9H_{10}O_3$, and tropine, $C_8H_{15}NO$, is formed from atropine, and oscine (scopoline), $C_8H_{13}NO_2$, from hyoscine-scopolamine ; the alkaloids can be partially regained from these products.   E. W. W.

Ketones of the Tropine Group. XII. Constitution of Ecgonine. By RICHARD WILLSTÄTTER and WILHELM MÜLLER (*Ber.*, 1898, **31**, 2655—2669. Compare Abstr., 1898, i, 603).—*Hydroecgonidineamide*, $C_8H_{14}N\cdot CO\cdot NH_2$, prepared by the action of ammonia on the ethylic salt of hydroecgonidine, crystallises in long, six-sided tablets melting at 126—127°. When this substance is heated with potassium hypobromite, it yelds *isotropylamine*,

$$\begin{array}{l} CH_2\cdot CH-CH\cdot NH_2 \\ \quad\quad NMeCH_2 \\ CH_2\cdot CH-CH_2 \end{array},$$

which is isomeric with the tropylamines formed by the reduction of tropinonoxime ; it is a colourless oil, which boils at 206—207° (corr.), and solidifies at 8·5°. The *mercurichloride* is soluble in hot water, and crystallises in characteristic tablets ; the *hydrochloride* crystallises in compact, six-sided tablets, and sublimes when carefully heated ; the *picrate* melts and decomposes at 236—237°, and the *platinochloride* decomposes at 261°, whilst the aurichloride could not be obtained of definite composition. The *thiocarbamide*, $NHPh\cdot CS\cdot NH\cdot C_8H_{14}N$, crystallises in colourless, swallow-tail forms, and melts at 138—139°. Nitrous acid does not convert the base into isotropine, but into tropidine. Isotropylamine can also be prepared from hydroecgonineamide by Curtius' method. The *hydrazide* forms a *picrate* melting at 172°, and, when treated with nitrous acid, yields *di-isotropylcarbamide*, from which isotropylamine can be prepared by the action of hydrochloric acid.

When ecgonine is oxidised by means of chromic acid, it yields tropinone, and this reaction shows that the hydroxyl group of ecgonine is in the same position as that of tropine and ψ-tropine. Moreover, since the properties of ecgonine are those of a β- and not of a γ-hydroxy-acid, it follows that ecgonine has the constitution I.

$$\text{I.} \begin{array}{l} CH_2\cdot CH-CH\cdot COOH \\ \quad\quad NMeCH\cdot OH \\ CH_2\cdot CH-CH_2 \end{array} \quad\quad \text{II.} \begin{array}{l} CH_2\cdot CH-CH\cdot COOH \\ \quad\quad NMeCH \\ CH_2\cdot CH-CH \end{array}$$
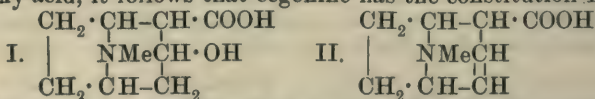
Anhydroecgonine, therefore, has the constitution II, which is in harmony with the formation from it of δ-cycloheptatrienecarboxylic acid melting at 32° ; this, as shown by its behaviour to alcoholic

potash (Einhorn and Willstätter, Abstr., 1895, i, 92), does not contain an ethylene linking in the Δ^1-position. A. H.

Alkaloidal Constituents of Cascarilla Bark. By WILLIAM A. H. NAYLOR (*Pharm. J.*, 1898, 59, 279).—Two bases are obtained by extracting the powdered bark with chloroform water containing 3 per cent. of oxalic acid. The one allied to choline forms a platinochloride crystallising in yellow, hexagonal plates, and a crystalline hydrochloride which gives off trimethylamine on heating; analysis of the former salt indicates that the base is in reality, not choline, but betaine. The second base, *cascarilline*, isolated for the first time, forms a buff-coloured *platinochloride*, which is soluble in alcohol and crystallises from water in prismatic plates. G. T. M.

Antipeptone. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1898, 26, 110—122. Compare Abstr., 1898, i, 611).—Antipeptone is not a peptone, neither is it a chemical unit (carnic acid) as alleged by Siegfried. It is a mixture of heterogeneous substances which, by means of phosphotungstic acid, can be divided into two parts, basic and acid. Among the bases, histidine, arginine, and another base of unknown nature were found; among the acids, aspartic acid was separated. W. D. H.

Guanylic Acid from Pancreas and its Decomposition Products. By IVAR BANG (*Zeit. physiol. Chem.*, 1898, 26, 133—159).— The *potassium* salt of guanylic acid, obtained by heating pancreas or nucleoproteid on the water-bath with 2 per cent. caustic potash, separates from the filtered extract as a voluminous sediment, which redissolves in hot water without decomposition, and is again precipitated as the solution cools. After repeating this treatment several times, the salt gives neither the Millon nor the biuret reaction. The free *guanylic acid* liberated by the addition of 5 per cent. acetic acid to the warm solution of the potassium salt, is obtained, after washing with alcohol and ether, in the form of a white powder. The other nucleic acids are not liberated from their salts by acetic acid, but in this case the free acid is obtained, and the use of acetic acid is preferable, since guanylic acid is slowly decomposed by hydrochloric acid at ordinary temperatures. Guanylic acid may be prepared directly from nucleoproteid by extraction with hot water, but the yield is smaller than by the above process. The free acid has a feebly acid reaction; it dissolves readily in alkalis and ammonia, and also in dilute mineral acids; its aqueous solution gives precipitates with solutions of the heavy metals, but not with albumin dissolved in dilute acetic acid, an acidic solution forms precipitates with phosphotungstic, tannic, and picric acids. Neither iron nor sulphur are present in guanylic acid; it contains less phosphorus and more nitrogen than the other nucleic acids, the ratio of these elements being P : 3N, whereas in the latter compounds it is P : 5N ; hence the latter ratio can no longer be regarded as characteristic of these compounds. The analytical results agree most closely with the formula $C_{22}H_{34}N_{10}P_2O_{17}$, and although it is unlike other nucleic acids in composition and in many of its properties, the products of its decomposition show it to be closely related

to this class of substances. On boiling guanylic acid with dilute mineral acids, it decomposes, yielding a substance belonging to the pentose group, guanine, phosphoric acid, and ammonia. The exact nature of the pentose derivative has not been determined; it reduces Fehling's solution, forms an osazone melting at 151—154°, is unfermentable, and cannot be obtained crystalline; the quantity produced, calculated in terms of glucose, amounts to about 30 per cent. of the original substance. Nine-tenths of the nitrogen originally present in guanylic acid is obtained, after hydrolysis, in the form of guanine; this is the first example of a nucleic acid giving rise to only one xanthine base, and it is on this account that the name guanylic acid is given to the compound.

The only other nitrogenous product of decomposition is ammonia; no trace of thymine could be obtained, either from guanylic acid or from nucleoproteid.   G. T. M.

Ovimucoid and a New Glucoproteid from Blood-serum. By CARLO U. ZANETTI (*Chem. Centr.*, 1898, i, 624—625; from *Ann. Chim. Farm.*, 26, 529—534. Compare Henriques, Abstr., 1897, 570).—The author attributes the reducing action of blood to the presence of a substance which is closely related to, or identical with, ovimucoid. Ovimucoid is prepared from egg-albumin by dissolving it in 10 times its volume of a 5 per cent. solution of sodium chloride, adding acetic acid, removing the albumin and globulin by coagulating, filtering, concentrating, and finally precipitating with alcohol. It can be purified by dissolving in water and precipitating with alcohol, the sodium chloride being removed by dialysing. The white, pulverulent mass contains $C = 48.75—48.94$, $H = 6.9—6.94$, $N = 12.46$, $S = 2.22$ per cent., and with hydrochloric acid gives glucosamine, and one third of its sulphur in the form of sulphuric acid. The serum of the blood of oxen yields a similar substance, possibly identical with ovimucoid.
E. W. W.

Existence of the Proteid Radicle suggested by Bertrand in the Oxydases. By JOSEPH DE REY-PAILHADE (*Bull. Soc. Chim.*, 1897, [iii], 17, 756—757).—It has been suggested by Bertrand (Abstr., 1897, ii, 493) that the oxydases contain a radicle of proteid character capable of entering into loose combination with manganese or hydrogen, and the author points out that philothion, a substance discovered by him in 1889 and subsequently described on many occasions, possesses the properties required of such a compound. The existence of philothion and analogous substances in animal tissues in the presence of manganese suggests a series of combinations and decompositions which offer a clear explanation of the mechanism of respiration in the tissues.   N. L.

Organic Chemistry.

Reductions in the Presence of Palladium. By Nicolai D. Zelinsky (*Ber.*, 1898, **31**, 3203—3205).—Experiments have previously been made with palladium-hydrogen as a reducing agent by Graham (*Annalen Sup.*, 1867, **5**, 1) and by Saytzeff (*J. prakt. Chem.*, 1872, [ii], **6**, 128); the author finds that it may be employed with great success in the reduction of iodides and bromides of cyclic alcohols, compounds which it has hitherto been impossible to reduce by any of the ordinary methods. Zinc filings are well washed with alcohol, then with dilute sulphuric acid until a vigorous evolution of gas begins, and finally with water; a 1—2 per cent. palladium chloride solution, which has been acidified with hydrochloric acid, is poured in and almost immediately a thin, adhesive layer of palladium is deposited on the zinc. This palladium–zinc couple, when washed with alcohol and, when necessary, dried, is ready for use. The reduction, as a rule, takes place readily at the ordinary temperature, but a temperature of 100° may also be employed. A flask filled to one-third with the zinc–palladium is provided with a reflux condenser and dropping funnel, the couple is partly covered with methylic or ethylic alcohol and hydrochloric acid saturated at 0° run in drop by drop, at first the hydrogen is absorbed by the palladium, but as soon as bubbles of the gas are evolved the bromide or iodide to be reduced may be added in small quantities, and then more hydrochloric acid, the quantities being so regulated that the reaction does not become too violent. In case any volatile hydrocarbon may be carried over, the gases evolved are bubbled through a wash bottle containing alcohol. The zinc–palladium remaining in the flask may be washed with hydrochloric acid and with alcohol, and is then ready for further use. J. J. S.

Decomposition of a Normal Saturated Hydrocarbon by Aluminium Chloride. By Charles Friedel and Alexandre Gorgeu (*Compt. rend.*, 1898, **127**, 590—594).—In extension of the work of Friedel and Crafts on the decomposition of aromatic hydrocarbons by aluminium chloride, the authors have investigated its action on pure normal hexane. This was heated on the water-bath, in successive small quantities, with well-powdered, freshly prepared aluminium chloride; on passing the products of the action, after removing the hydrogen chloride formed, through a U-tube cooled by a freezing mixture, a mobile liquid condensed which consisted principally of pentane, boiling at 35°. The gases formed in the action were collected over mercury, and found to consist principally of normal butane, identified by its boiling point and solubility in amylic alcohol; a small quantity of propane was, however, also present. The action thus consisted essentially in the substitution of successive methyl groups, at the end of the chain, by hydrogen atoms. In addition to the hydrocarbons isolated, richer in hydrogen than hexane, products richer in carbon were probably formed; on treating the aluminium chloride

used with water, and shaking with ether, a brownish, viscous liquid was obtained, which was, however, not further investigated.

The solubility in amylic alcohol of the paraffins gaseous at ordinary temperatures was determined as a means of recognising their presence in the gaseous product obtained in the above work; in using amylic alcohol for dissolving gases, care must be taken that the air, which it dissolves to the extent of 10 per cent., has been previously expelled by boiling. The methane and ethane employed were prepared by decomposing mercury-methyl and mercury-ethyl at 70—80° by dilute sulphuric acid from which air had previously been expelled; the propane and butane were obtained respectively from isopropylic and secondary butylic iodide by the action of zinc in presence of a very small quantity of hydrochloric acid, and were freed from hydrogen by being dissolved in amylic alcohol and subsequently liberated by heating. The solubilities are as follows: 1 vol. of amylic alcohol boiling at 130—132° dissolves, at 12·5°, 0·05 vol. of hydrogen under a pressure of 750 mm., and 0·5 vol. of methane under normal pressure; whilst 3·3 vols. of ethane are dissolved at 14°, and 12 vols. of propane at 16° under a pressure of 750 mm. Under a pressure of 760 mm., 11 vols. of propane are dissolved at 23°, and 44 vols. of butane at 22°, whilst 72 vols. of the latter gas are dissolved at 13° under a pressure of 740 mm.   W. A. D.

Synthesis of Ethylic Alcohol. By FRANK WOOD (*Chem. News*, 1898, **78**, 308).—Alcohol was not obtained under the following circumstances. When acetylene, from calcium carbide, and hydrogen were passed though a calcium chloride tube, then through 18 inches of red hot combustion tube containing asbestos wool, and finally into pure sulphuric acid either cold or heated to 170°, the acid being then diluted largely and distilled; or when the gases from the action of dilute sulphuric acid on a mixture of calcium carbide and zinc dust, or of copper acetylide and zinc dust were treated in a similar manner, or when the gas evolved from the action of ammonia on the mixture of copper acetylide and zinc dust was passed into strong sulphuric acid, &c.   D. A. L.

Normal Cyanobutylic Alcohols. By LOUIS HENRY (*Chem. Centr.*, 1898, i, 984—985; from *Bull. Acad. roy. Belg.*, [iii], **35**, 173—181).—a-*Hydroxybutyronitrile* (a-*cyanopropylic alcohol*), prepared from hydrocyanic acid and propaldehyde, is a rather viscous, colourless liquid with a bitter-sweet taste, has a sp. gr. = 1·0238 at 11°, and is insoluble in carbon bisulphide but soluble in water, alcohol, ether, chloroform, benzene, and acetone. It easily unites with amido- and imido-bases with loss of water, and when heated, decomposes into hydrogen cyanide and propaldehyde. The *acetyl* derivative, $CN \cdot CH(OAc) \cdot CH_2Me$, prepared by the action of acetic anhydride and acetic chloride on the nitrile, boils at 185—186°. β-*Hydroxybutyronitrile* (β-*cyanoisopropylic alcohol*) is obtained by the action of potassium cyanide on propylene monobromhydrin or iodhydrin; it is a rather viscous, colourless liquid with a faint odour and sweetish taste, boils at 220—221° under 757 mm., and at 123—125° under 22 mm. pres-

sure, is soluble in water, alcohol, and ether, insoluble in carbon bisulphide, and does not react with amido- or imido-bases. The *acetate* boils at 210° under 765 mm. pressure. The *ethoxy*-derivative boils at 173—174°. *γ-Hydroxybutyronitrile* (*γ-cyanopropylic alcohol*) can be prepared by the action of potassium cyanide on trimethylene iodhydrin, or from γ-chlorobutyric acid by hydrolysing the acetate by means of powdered sodium or potassium hydroxide, and distilling under diminished pressure ; it is a rather viscous, colourless oil with a sharp, pungent taste and faint odour, is soluble in water, alcohol, ether, and chloroform, but insoluble in carbon bisulphide, has a sp. gr. = 1·0290 at 8°, and boils at 238—240° under 765 mm., at 150—151° under 68 mm., and at 140° under 30 mm. pressure. It gives the reactions of an alcohol and a nitrile, but does not act on amines or imines. The *ethoxy*-derivative boils at 185° and the *acetate* at 237°. *γ-Chlorobutyronitrile* boils at 195°, the corresponding *bromo*-derivative at 213—214°, and the *iodo*-derivative at 230°.

E. W. W.

Chlorine Derivatives of Nitriles containing Three and Four Carbon Atoms and their Volatility. By LOUIS HENRY (*Chem. Centr.*, 1898, ii, 22 ; from *Bull. Acad. roy. Belg.*, [iii], **35**, 360—367).—*a-Chloropropionitrile*, prepared by the action of phosphorus pentachloride on the nitrile of ordinary lactic acid, is a colourless liquid, boils at 122—123° under a pressure of 744 mm., and has a sp. gr. = 1·0792 at 10°. *β-Chloropropionitrile*, obtained in a similar way from the nitrile of ethylenelactic acid, boils at 174—176° under a pressure of 752 mm., and has a sp. gr. = 1·1443 at 18·5°. The nitriles of *a*- and *β*-hydroxybutyric acid yield *a-chlorobutyronitrile* and *β-chlorobutyronitrile* respectively ; the former is a colourless liquid, boils at 142—143°, and has a sp. gr. = 1·0440 at 9° ; the latter boils at 175—176°, and has a sp. gr. = 1·0772 at 9°. *γ-Chlorobutyronitrile*, prepared by the action of potassium cyanide on trimethylene chlorobromide, boils at 195° and has a sp. gr = 1·1620 at 11°. The vapour densities of the above compounds were determined, and their boiling points show that the presence of chlorine and nitrogen in a molecule decreases the boiling point, this effect being the most marked when the nitrogen and chlorine atoms are united to the same carbon atom. E. W. W.

Alkylic Borates : Properties of Triethylic Borate. By H. COPAUX (*Compt. rend.*, 1898, **127**, 719—722).—When triethylic borate is treated with chlorine in the cold, a gelatinous mass is obtained which carbonises on warming, and yields trichlorether, $CHCl_2 \cdot CHCl \cdot OEt$, when hydrolysed with potash. Triethylic borate added to a solution of sodium ethoxide in absolute alcohol produces a crystalline deposit ; this *compound* has the composition $B(OEt)_3, NaOEt$, but is not a simple additive product, for it does not regenerate the ethereal salt on heating to 200°, neither does it form ether when digested with ethylic iodide at 140°. The author suggests that the substance contains quinquevalent boron and has the constitution $Na \cdot B(OEt)_4$. G. T. M.

Compounds of Carbonic Anhydride with Ethylic Ether and Alcohols. By WALTHER HEMPEL and JOHANNES SEIDEL (*Ber.*, 1898, 31, 2997—3001).—See this vol., ii, 151.

Conversion of Geraniol into Methylheptenol. By FERDINAND TIEMANN (*Ber.*, 1898, 31, 2989—2992).—The substance obtained by Barbier (Abstr., 1898, i, 617) by heating geraniol ("lemonol") with concentrated alcoholic potash at 150° under pressure, and named by him dimethylheptenol, is found to be no other than methylheptenol ("methylhexylenecarbinol"; Abstr., 1894, i, 84; Wallach, Abstr., 1893, i, 598), now formulated as $CMe_2:CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot OH$. When linalool is treated in the same way, it is hardly altered.

<div align="right">C. F. B.</div>

Epidibromhydrins. By ROBERT LESPIEAU (*Ann. Chim. Phys.*, 1897, [vii], 11, 232—288).—This is a very long paper, consisting, for the most part, of a detailed account of work already published (Abstr., 1893, i, 1; 1896, i, 332; 1898, i, 116). Two isomeric *tribromopropylic alcohols* are described; $CH_2Br\cdot CBr_2\cdot CH_2\cdot OH$, produced by adding bromine to the alcohol, $CH_2:CBr\cdot CH_2\cdot OH$, forms a syrupy liquid which boils at 125—129° under a pressure of 18 mm.; $CHBr_2\cdot CHBr\cdot CH_2\cdot OH$, obtained from $CHBr:CH\cdot CH_2\cdot OH$ (Abstr., 1897, i, 209), resembles its isomeride, and boils at 155—157° under 27 mm. pressure.

Dibromallylic alcohol, $CHBr:CBr\cdot CH_2\cdot OH$, which results from the action of sodium methoxide on $CH_2Br\cdot CBr_2\cdot CH_2\cdot OH$, boils at 205—208° under standard pressure; its *methylic* ether, $CHBr:CBr\cdot CH_2\cdot OMe$, boils at 175—177° under 745° mm.; its sp. gr. = 1·903 at 0°.

Tetrabromopropylic alcohol, $CHBr_2\cdot CBr_2\cdot CH_2\cdot OH$, produced by adding bromine to the preceding alcohol in chloroform solution, is obtained as a viscid liquid boiling at 164—168° under 20 mm.; its *methylic* ether boils at 140—145° under the same pressure.

Iodopropargylic alcohol (iodopropinol), $CI:C\cdot CH_2\cdot OH$, obtained by the action of a solution of iodine in potassium iodide on the cuprous derivative of propargylic alcohol (propinol), separates from the ethereal extract in colourless, nacreous crystals melting at 43—44°; it turns pink after a time. It is soluble in water, but when boiled with this solvent, undergoes a change, and crystals melting at 150° are obtained. The *methylic* ether melts at 24°, and boils at 74° under 20 mm. pressure.

Diacetylene glycol (hexadiinediol), $OH\cdot CH_2\cdot C:C\cdot C:C\cdot CH_2\cdot OH$, produced by the oxidation of the cuprous derivative of propargylic alcohol with potassium ferricyanide, crystallises in colourless needles melting at 111—112°, and dissolves in all the usual organic solvents except petroleum; it is rapidly coloured on exposure to light, and becomes partly insoluble. A chloroform solution of bromine is rapidly decolorised by the glycol (4Br being absorbed per molecule of glycol). The *diacetyl* derivative, obtained by heating it with acetic anhydride and zinc chloride, melts at 35°. The *dimethylic* ether, prepared from the cuprous derivative of methylic propargylic oxide, is a colourless liquid at ordinary temperatures; it melts at −9°, has a sp. gr. = 0·9969 at 0°, and refraction $n_D = 1·494$.

<div align="right">G. T. M.</div>

A New Sugar accompanying Sorbitol. By CAMILLE VINCENT and JEAN MEUNIER (*Compt. rend.*, 1898, **127**, 760—762). —When sorbitol is obtained from the juice of certain rosaceous fruits, the mother liquor, after the crystallisation of this substance, contains a homologous alcohol not hitherto described. The solution is submitted to the action of the sorbose bacterium, in order to destroy any remaining sorbitol, and then concentrated to a syrupy consistency and treated with benzaldehyde; the *dibenzylidene* compound, $C_8H_{14}O_8(CHPh)_2$, of the new alcohol which separates, is insoluble in water, but dissolves in chloroform and alcohol, and crystallises from the former solvent in needles melting at 230°. The *octitol*, $C_8H_{18}O_8$, regenerated from the benzylidene compound, is an uncrystallisable syrup which loses 18 per cent. in weight when heated at 110° under reduced pressure; on exposing the desiccated substance to the air for 3 days, 10 per cent. of moisture is regained. Its specific rotation at 20° is $a_j = -3.42°$; the addition of an alkaline solution of borax trebles the rotation without change of sign. The *acetyl* derivative, obtained by heating the syrup with excess of acetic anhydride in the presence of zinc chloride, crystallises from alcohol in tabular crystals and melts at 119°. The physical properties of the new alcohol and its derivatives differ greatly from those of sorbitol and its derivatives, and the paper concludes with a table of comparisons. G. T. M.

Rôle of Pentosans in the Manufacture of Crude Sugar. By ANTON STIFT, and by K. KOMERS and ANTON STIFT (*Bied. Centr.*, 1898, **27**, 849—851; from *Oesterr. Zeit. Zuckerind.*, 1897, 1018, and 1898, 6. Compare Abstr., 1898, i, 229).—Extracted diffusion sections of sugar-beet contain considerable amounts of pentosans, only a portion of which passes into the juice. In crude sugar, the pentosans may amount to as much as two-thirds of the organic non-sugar present, but owing to their sparing solubility only a small quantity passes into the green syrup. The pentosans which pass into the juice are not decomposed in the least by the operations employed in purification, &c. It remains uncertain whether the slight reducing power of crude sugar is due to the presence of pentosans, but there certainly seems to be some relation between the amount of pentosans and the reducing power. The amount of sugar in fresh sections changes very quickly; even in one day, the amount of saccharose diminishes considerably, whilst an appreciable amount of invert-sugar is produced.

N. H. J. M.

Combination of Lithium Chloride with Methylamine. By J. BONNEFOI (*Compt. rend.*, 1898, **127**, 516—519. Compare Abstr., 1897, ii, 37, and this vol., ii, 96).—Methylamine is rapidly absorbed by dry and porous lithium chloride, the composition of the product depending on the temperature.

The compound $LiCl,NH_2Me$ is formed above 65° by direct combination, or by the action of heat on the other compounds. Its heat of dissolution is $+ 6.66$ Cal., and hence LiCl sol. $+ NH_2Me$ gas $= LiCl,NH_2Me$ solid develops $+13.82$ Cal. Its vapour pressure is 505 mm. at 66.2°, 642 mm. at 71°, and 819 mm. at 74.4°.

The compound $LiCl,2NH_2Me$ is formed between 40° and 65°; its heat of dissolution is + 6·647 Cal., and its heat of formation from its proximate constituents + 25·88 Cal. Its vapour pressure is 149 mm. at 27°, 347 mm. at 40°, and 642 mm. at 50·2°.

The compound $LiCl,3NH_2Me$ is formed below 40°, and no compound containing more methylamine could be obtained even by using the liquefied gas. Its heat of dissolution is + 7·885, and its heat of formation + 36·69 Cal. Its vapour pressure is 289 mm. at 22·4°, 600 mm. at 35°, and 827 mm. at 40·5°.

In all cases, the heat of formation calculated by means of Clapeyron's formula agrees closely with the number directly determined.

The heat of dissolution of methylamine at about 12° is + 12·05 Cal.

<div align="right">C. H. B.</div>

Formation of Putrescine (Tetramethylenediamine) from Ornithine. By ALEXANDER ELLINGER (*Ber.*, 1899, **31**, 3183—3186). —Ornithine hydrochloride was dissolved in about 100 times its weight of water, and the solution made faintly alkaline with soda and sewn with a little putrefying pancreas; the whole was then left for 3 days at 30°, made faintly acid with acetic acid, heated to boiling, and filtered. The filtrate was shaken with benzoic chloride and soda, when the dibenzoyl derivative of tetramethylenediamine, melting at 176°, was precipitated. The base may also be isolated by Brieger's method, in which case the platinochloride is formed as an intermediate step.

The above mode of preparation of putrescine disposes of Baumann's theory that the substance is produced by an oxidation of ethylamine. The reaction is evidently expressed by the equation

$$NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH = CO_2$$
$$+ NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2,$$
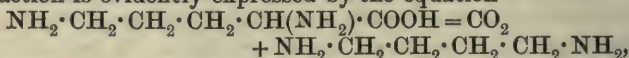
and the production of carbonic anhydride is confirmed by an examination of the gases evolved during the process.   A. L.

Amines and Amides Derived from Aldehydes. By MARCEL DELÉPINE (*Compt. rend.*, 1898, **127**, 622—625).—In a series of previous papers (Abstr., 1897, ii, 87, 131, and 359; 1898, i, 363, 415, and 462; ii, 368, 501, and 559), the author has given the thermochemical data involved in the combination between certain aldehydes and ammonia, or certain amines. The data obtained are now classified, and generalisations drawn from them.

I. The interaction of liquid aldehydes with $1NH_3$ diss. to form solid derivatives gives rise to less than 13·7 Cal. in the case of benzoic, anisic, pyromucic, and acetic aldehydes; from this, it follows that hydrogen chloride, which generates 13·7 Cal. in combining with NH_3 diss., will decompose the derivatives obtained in all these cases into the original aldehyde and ammonium chloride. Experiment verifies this conclusion.

II. The interaction of aromatic aldehydes and aqueous ammonia to form, not the hydramides, but the isomeric glyoxalidines, gives a thermic value $\geqq 17$ Cal., which excludes the possibility of decomposing the bases formed by acids; a study of the salts of furfurine shows that this stability is maintained in presence of very concentrated acids.

Hydrocinnamide, usually classed as a hydramide, is more probably a glyoxalidine. From the equation

$$C_{15}H_{12}N_2O_3,HCl \text{ sol.} + HCl \text{ in } 3H_2O = 3C_5H_4O_2 \text{ liq.} + 2NH_4Cl \text{ sol.} - 8\cdot5 \text{ Cal.}$$

Furfurine hydrochloride.   Furfuraldehyde.
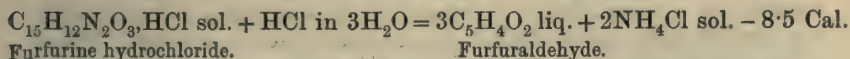
it appears that the reverse change, involving the decomposition of ammonium chloride by furfuraldehyde with the formation of furfurine hydrochloride, should be possible. This view was strikingly confirmed by carrying out the analogous decomposition of ammonium chloride by benzaldehyde; this takes place at 180—185°, and gives rise to amarine hydrochloride and aqueous vapour.

III. The elimination of water between an aldehyde and a pyridine or quinoline base is accompanied by a heat development of 15, 30, or 40 Calories; taking into account the fact that the product has a basicity nearly equal to that of the original base, an explanation is afforded of its stability towards hydrolytic agents.

IV. From the heat of formation of hexamethylenetetramine (Abstr., 1897, ii, 359), the latter appears to occupy, as regards stability, a position between the glyoxalidines and the hydramides; like the former, it yields salts with acids, but is decomposed, like the latter, when the proportion or concentration of the acid is increased. This decomposition, however, is limited by the fact that formaldehyde is capable of decomposing ammonium salts (compare *Bull. Soc. Chim.*, 1895, [iii], 13, 163, and Cambier and Brochet, Abstr., 1895, i, 641). In order to isolate the base thus formed, the following systems were studied.

(1) $6CH_2O + 4NH_4Cl + I_n$ in KI   Both gave rise to
(2) $6CH_2O + (4NH_4I + I_4 = 1^{\text{lit.}})$ $C_6H_{12}N_4,CH_2O,HI,I_{3 \text{ to } 4}$.
(3) 6 to $16CH_2O + (4NH_4I + HgI_2 = 1^{\text{lit.}})$ gave
                $5(C_6H_{12}N_4,CH_2O),6HI,4HgI_2$ (m. p. = 184°).
(4) $6CH_2O + (4NH_4Cl + HgCl_2 = 1^{\text{lit.}})$ gave
                $2(C_6H_{12}N_4,CH_2O),2HCl,3HgCl_2$ (m. p. = 145°).

In all cases, homogeneous crystals separated; it is remarkable that, in all the compounds formed, the ratio $C : N = 7 : 4$. That the compounds obtained are the result of an antagonistic equilibrium is shown by the fact that, on adding $I_n + KI$ to the system $C_6H_{12}N_4 + 4HCl$, the amount of the salt $C_6H_{12}N_4,CH_2O,HI,I_n$ obtained is the same as that given by equation (1) alone under similar conditions of concentration. Although the thermic values indicate that formaldehyde should be capable of completely displacing hydrogen chloride in ammonium chloride, this is not the case practically, owing to the fact that hexamethylenetetramine commences to dissociate at 100° into formaldehyde and ammonia.   W. A. D.

Isomeric Salts of Ethylnitrolic Acid. By Otto Graul and Arthur Hantzsch (*Ber.*, 1898, 31, 2854—2879).—According to V. Meyer, the nitrolic acids are to be regarded as nitroximes, $NO_2 \cdot CR:N \cdot OH$, and one of their characteristics is the formation of intense red solutions when treated with alkali. The authors have succeeded in isolating these red salts, which they term *erythro*-salts. They correspond with the general formula $C_2H_3N_2O_3M'$; they crystallise well, are extremely explosive and unstable, and when treated with dilute acids

are at once reconverted into colourless ethylnitrolic acid. When warmed, or, still better, when placed in direct sunshine, the red salts are converted into a second series of colourless or *leuco*-salts isomeric with the erythro-salts, and a similar change takes place in solution. These leuco-salts cannot be reconverted into the erythro-salts nor yet into the free nitrolic acid, and the acid from which they may be supposed to be derived has not been isolated. Both series of salts undergo practically no hydrolysis in aqueous solution, and they are isomeric, not polymeric. Indications of the existence of a third series of isomeric salts, also colourless, have been met with; they are obtained under certain conditions from the nitrolic acid or from the red salts as amorphous powders, but all attempts to obtain them in a pure form have been unsuccessful, as even below 0° they change back into the red salts. A series of intensely yellow salts has also been obtained. These correspond to the general formula $C_2H_3N_2O_3M' + C_2H_4N_2O_3$, and may be termed *acid* salts; they are formed by the action of an alkali (1 mol.) on the acid (2 mols.) in concentrated alcoholic solutions and at low temperatures, are very unstable, and in the solid form readily decompose into the red salts and free nitrolic acid. Ethers of the erythro- and leuco-salts can only be obtained by the aid of the silver salts; the ethers obtained from the leuco-silver salts are all oils.

The two isomeric series of salts, erythro- and leuco-, yield the same products on treatment with acid, namely, hydroxylamine, acetic and nitrous acids, and nitrous oxide. The erythro-salts, on treatment with alkalis, yield acetic and nitrous acid, and the leuco-salts, aldehyde. When reduced with sodium amalgam, the erythro-salts and also the free acid yield nitrous acid, ammonia, acetic acid, and azaurolic acid (Abstr., 1883, 40). Under the same treatment, the leuco-salts yield nitrous acid, ammonia, and aldehyde.

Potassium erythronitrolate, when treated at a very low temperature with bromine, yields a blue, unstable oil, which at a somewhat higher temperature becomes converted into Ter Meer's bromodinitroethane (this Journ., 1876, i, 68). The blue compound is considered to be bromonitronitrosoethane, $NO_2 \cdot CBrMe \cdot NO$.

The leuco-salts yield yellow or brown bromine derivatives; with an excess of bromine, a compound, $C_2H_3N_2O_3Br_3$, is obtained, but this readily loses two atoms of bromine and becomes converted into the yellow solid compound, $C_2H_3N_2O_3Br$, which is very sparingly soluble in all ordinary solvents, and is probably a polymeride of the above-mentioned bromonitronitrosoethane.

The authors suggest the following constitutions.

1. Nitroisonitroso-derivatives, free acid, benzoyl derivative, and white, amorphous potassium salt, $NO_2 \cdot CMe{:}N \cdot OR$.

2. Isonitronitroso-derivatives, the stable leuco-salts, $NO \cdot CMe{:}NO_2M'$.

3. Erythro-salts, $CMe\underset{NO(OM')}{\overset{N\text{------}}{<}}{>}O$, and arguments in favour of these constitutions are given in detail.

Ethylnitrolic acid itself is a very feeble acid, and may be compared with phenol or acetophenoneoxime. The erythro-salts are derivatives of a much stronger acid and undergo little or no hydrolysis in aqueous

solution ; the following have been prepared, *potassium, sodium, silver, lead,* and *mercuric* erythronitrolates. J. J. S.

The Rendering Active ("Activirung") of Oxygen. Part III. Oxidation of Triethylphosphine. By CARL ENGLER and J. WEISSBERG (*Ber.*, 1898, **31**, 3055—3059).—The peroxide of turpentine has been shown (this vol., i, 221) to be destroyed at 140—160°, further oxidation of the turpentine taking place, and it is probable that a similar secondary action occurs at ordinary temperatures in the case of triethylphosphine, so that the oxidising action of the initial product is only observed after all free triethylphosphine has disappeared ; once the activity is manifested, however, it is more or less permanent. It is shown, by means of tests similar to those used in the case of the product from turpentine, that the oxidising power is not due to hydrogen peroxide or ozone.

The authors have examined the products of the action of dry oxygen on triethylphosphine. The crude liquid deposits crystals at −10°, or forms a solid, crystalline mass ; the crystals have the composition of triethylphosphine oxide, $POEt_3$, whilst the liquid seems to be a mixture of ethylic diethylphosphinate, $POEt_2 \cdot OEt$, with diethylic ethylphosphinate, $POEt(OEt)_2$, and, possibly, also triethylic phosphinate, $PO(OEt)_3$ (compare Jorissen, Abstr., 1897, ii, 253). When the liquid is hydrolysed with baryta water, an odour of triethylphosphine is noticeable, whilst alcohol and aldehyde-like substances may be driven over by distillation ; the non-volatile portion, on evaporation, deposits the pure barium salt of diethylphosphinic acid and an impure salt of monethylphosphinic acid.

The initial stage of the oxidation is supposed to be the formation of the peroxide, $\begin{smallmatrix} O \\ O \end{smallmatrix}\!\!>\!\!PEt_3$, which then suffers isomeric change, or reacts with unaltered triethylphosphine.

The analyses of the crude autoxidation product confirm the authors' original observation that rather less than one molecular proportion of oxygen is absorbed. This is not in agreement with the results of Jorissen (*loc. cit.*), but the discrepancy is, no doubt, due to the higher temperatures employed by that chemist. A. L.

Identity of the four Affinities of Sulphur in Sulphines. By A. BRJUCHONENKO (*Ber.*, 1899, **31**, 3176—3182).—Feebly active ethylic isoamylic sulphide ($[a]_D = +3.41$ at 18·5°) was treated with a molecular proportion of methylic iodide at ordinary temperatures. The *methylethylisoamylsulphine iodide*, $C_5H_{11} \cdot SMeEtI$, thus formed, was obtained in the form of regular, transparent needles ; it decomposed spontaneously, even when kept in a vacuum and in the dark ; when treated with cold nitric acid, it lost iodine, but did not yield sulphuric acid when heated with fuming nitric acid at 170—180° during several hours. It was optically active, its specific rotation being $[a]_D = +4.88$ at 18°, and it gave a thick, oily precipitate with cadmium iodide.

Active *methylethylamylsulphine iodide*, $C_5H_{11} \cdot SMeEtI$, was made by two different methods, namely, by the action of methylic iodide on ethylic amylic sulphide ($[a]_D = +14.71$ at 19°), and by the action of ethylic iodide on methylic amylic sulphide ($[a]_D = +13.24$ at 20°). In both

cases, the substance was obtained as a semi-crystalline syrup, soluble in water and alcohol, but insoluble in ether and benzene, and having a specific rotation $[a]_D = 13\cdot9$ at $19°$; the concentration of the solution was found to have little effect on the rotatory power.

As the preparation of these two substances has been carried out under conditions which render the occurrence of any isomeric change improbable, their identity may be regarded as further evidence of the equality of the four affinities of sulphur.

The proximity of the rotatory powers of the sulphides and the derived sulphine iodides would lead to the surmise that the latter are monomolecular, and this supposition is confirmed by determinations of their molecular weights.   A. L.

Derivatives of Natural Methylheptenone. By GEORGES LÉSER (*Compt. rend.*, 1898, **127**, 763—764. Compare Abstr., 1898, i, 617).— When a mixture of ethylic acetate and methylheptenone is treated with sodium and the product distilled under a pressure of 15—16 mm., the lower fraction boiling at $115°$ consists of acetylmethylheptenone, whilst that distilling between $130°$ and $200°$ contains a substance, produced by the condensation of two molecules of methylheptenone, accompanied by an elimination of one molecule of water, to which the name *bis-methylheptenone* is provisionally given; it boils at $172—174°$ under a pressure of 16 mm.

Acetylmethylethylheptenone results from the action of ethylic iodide on the sodium derivative of acetylmethylheptenone in alcoholic solution; it boils at $133—135°$ under a pressure of 15 mm. *Methylnonenone*, $CMe_2\!:\!CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2Et$, produced by boiling the preceding compound with aqueous potash, boils at $203—205°$ under ordinary pressure. *Ethylic methylhexenonepyruvate* (*ethylic 2-methyl-6 : 8-dione-2-noneoate*), $CMe_2\!:\!CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot CO\cdot COOEt$, formed on mixing together alcoholic solutions containing molecular proportions of methylheptenone, ethylic oxalate, and sodium ethoxide, is obtained in the form of its *copper* derivative, $Cu(C_{12}H_{17}O_4)_2$, which separates in olive-green needles when the crude product is added to a solution of copper acetate. The ethereal salt, obtained on decomposing the copper derivative with dilute sulphuric acid, boils at $164—165°$ under a pressure of 16 mm.   G. T. M.

Direct Oxidation of Fat. By MAURICE HANRIOT (*Compt. rend.*, 1898, **127**, 561—563).—When ozone is passed over neutral fat, an increase of 23 per cent. in the weight of the latter occurs; acetic acid appears to be formed in small quantity, together with other fatty acids which were not identified; formic acid, however, is not formed, or oxalic acid, sugar, starch, or cellulose. No details of the nature of the fat employed are given.   W. A. D.

Conversion of Geranic Acid into Citronellic Acid. By FERDINAND TIEMANN (*Ber.*, 1898, **31**, 2899—2903).—The synthesis of methylheptenone, $CMe_2\!:\!CH\cdot CH_2\cdot CH_2Ac$, and of geranic acid has already been described (Abstr., 1894, i, 84), and also the conversion of geranic acid into terpenes and their derivatives (*ibid.*, 1895, i, 639).

Geranic acid, $CMe_2\!:\!CH\cdot CH_2\cdot CH_2\cdot CMe\!:\!CH\cdot COOH$, is not reduced to citronellic acid, $CMe_2\!\cdot\!CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot COOH$, when

boiled with water and sodium amalgam, but is reduced when sodium (20 grams) is added to a solution of geranic acid (20 grams) in boiling amylic alcohol. The yield of citronellic acid is over 60 per cent.

Citronellonitrile, obtained from citronellaldoxime, is not readily hydrolysed by alcoholic potash; when boiled for 5—6 hours with a 15 per cent. alkaline solution, and then diluted with water, *citronellamide* is precipitated; it crystallises from light petroleum in colourless needles melting at 81·5—82·5°, and is only sparingly soluble in water, but dissolves readily in most organic solvents.

Citronellaldehyde is obtained when a mixture of calcium formate and citronellate is strongly heated; the yield is not good.

<div align="right">J. J. S.</div>

Transformation of Unsaturated α-Hydroxy-acids into Hydrofurfurancarboxylic Acids. By RUDOLPH FITTIG (*Annalen*, 1898, **303**, 165—171. Compare Abstr., 1898, i, 196).—It has been shown by the author that hot, dilute hydrochloric acid or caustic soda transforms unsaturated α-hydroxy-acids of the type

$$CHR\!:\!CH\cdot CH(OH)\cdot COOH$$
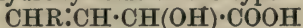
into the isomeric α-ketonic acid having the constitution

$$CH_2R\cdot CH_2\cdot CO\cdot COOH.$$
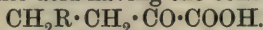
It was not found possible to trace the intermediate stages of the change, and, in order to gain information on this point, the author has studied the behaviour of an acid in which the ethylenic linking is further removed from the carboxylic group. The results are described in the following abstract. M. O. F.

Methylallyllactic Acid and Dimethylhydrofurfurancarboxylic Acid. By RUDOLPH FITTIG and HAROLD DE HAVEN-BOYD (*Annalen*, 1898, **303**, 171—183).—*α-Methylallyllactic acid*,

$$CH_2\!:\!CH\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot COOH,$$
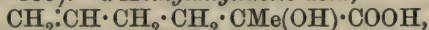
produced by hydrolysing the nitrile obtained from allylacetone and hydrogen cyanide, is a colourless, viscous liquid which decreases slightly in weight when preserved in a vacuum, probably owing to the formation of anhydride. The *calcium* salt crystallises in white leaflets containing $1\frac{1}{2}H_2O$; it dissolves more readily in cold water than in hot. The *barium* salt crystallises in anhydrous needles; the *silver* salt is very readily soluble in water. The *amide* crystallises in large, colourless, monoclinic plates and melts at 71°. The acid resists the action of sodium amalgam, and of boiling aqueous soda.

α-Methyldibromo-β-propyllactic acid,

$$CH_2Br\cdot CHBr\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot COOH,$$
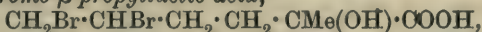
obtained by adding bromine to the foregoing acid dissolved in chloroform, crystallises in colourless prisms and melts at 107°.

Dimethylhydrofurfurancarboxylic acid, $\begin{array}{l} CH_2\cdot CH_2\cdot CMe\cdot COOH \\ CHMe\!-\!\!-\!O \end{array}$, prepared by heating calcium methylallyllactate with hydrochloric acid, is a colourless, volatile liquid which boils at 228°. The *calcium* salt contains $2H_2O$, and the *barium* and *silver* salts are anhydrous. The acid is indifferent towards sodium amalgam, and does not unite with bromine. On distilling an intimate mixture of the calcium salt with lime, methyl butyl ketone is obtained. M. O. F.

Basic Copper Compounds of Ethylic Acetoacetate and Ethylic Benzoylacetate. By WILHELM WISLICENUS (*Ber.*, 1898, 31, 3151—3158).—Ethylic cupro-acetoacetate can be advantageously prepared by agitating an ethereal solution of ethylic acetoacetate with copper acetate solution. The copper compound crystallises from benzene in green needles, and melts at 192—193°, whereas Conrad (Abstr., 1878, 26) gives the melting point as 182°. When the copper compound is boiled with methylic alcohol, ethylic acetoacetate is set free, and a *basic copper methoxide* of *ethylic acetoacetate*,

$$OMe \cdot Cu \cdot O \cdot CMe \vdots CH \cdot COOEt,$$
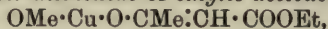
is produced, which crystallises from methylic alcohol in small, blue needles and melts and decomposes between 156° and 175°. The reaction is not complete, but leads to a state of equilibrium between the green and blue salts, which is largely influenced by the relative proportions of ethylic acetoacetate and methylic alcohol present. The blue compound is reconverted into the green salt when it is warmed with an equivalent of ethylic acetoacetate. The same change occurs when the blue compound is boiled with benzene, and it is probable that, in this case, cupric methoxide, $Cu(OMe)_2$, is also produced. Ethylic cuprobenzoylacetate, which melts at 182—183°, also undergoes a similar change when boiled with methylic alcohol, a *basic methoxide* being produced which crystallises in blue, microscopic needles.

<div align="right">A. H.</div>

Action of Cyanogen on Ethylic Acetoacetate and Acetylacetone. By WILHELM TRAUBE (*Ber.*, 1898, 31, 2938—2946. Compare Abstr., 1898, i, 241).—When cyanogen is passed into a well-cooled alcoholic solution of ethylic acetoacetate containing only a small amount of sodium ethoxide, a crystalline precipitate is produced which consists of *ethylic a-acetyl-β-cyano-β-imidopropionate*, or *ethylic dicyanacetoacetate*, $NH \vdots C(CN) \cdot CHAc \cdot COOEt$, melting at 122°; this substance has acid properties and dissolves in alkalis, but the solutions rapidly decompose, ethylic cyanacetoacetate, melting at 36°, being formed. If the alcoholic solution of ethylic acetoacetate is not cooled during the treatment with cyanogen, *ethylic aa-diacetyl-ββ-di-imidoadipate*, or *ethylic dicyanodiacetoacetate*, $C_2(NH)_2(CHAc \cdot COOEt)_2$, is produced, and the latter is also formed by the action of ethylic acetoacetate and a little sodium ethoxide on the foregoing compound. It crystallises in colourless needles, melts at 132°, and dissolves in aqueous soda, forming a yellowish-red solution, from which acids precipitate *monethylic di-imidoacetylmethylcyclopentenedicarboxylate*, $C_{12}H_{14}N_2O_5$, which crystallises in dark yellow needles melting at 136°. Ethylic dicyanacetoacetate is converted by ethylic malonate, in the presence of a small amount of sodium ethoxide, into *ethylic a-carboxyl-a'-acetyl-ββ-di-imidoadipate*, $C_{15}H_{22}N_2O_7$, which forms compact crystals melting at 93°.

Cyanimidomethylacetylacetone, or *dicyanacetylacetone*,
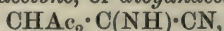
$$CHAc_2 \cdot C(NH) \cdot CN,$$

prepared in a similar manner to the corresponding derivative of ethylic acetoacetate, crystallises in plates melting at 129—131°. Its solution in aqueous soda readily decomposes, forming *cyanacetylacetone*, $CHAc_2 \cdot CN$,

which crystallises in large, colourless plates melting at 50°, and is a strong acid, decomposing carbonates and acetates. *Dicyanodiacetylacetone*, or *symmetrical αα-tetramethyl-ββ-di-imidobutane*,
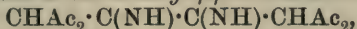
$$CHAc_2 \cdot C(NH) \cdot C(NH) \cdot CHAc_2,$$

which can also be obtained in a similar manner to the corresponding derivative of ethylic acetoacetate, crystallises in pale yellow tablets melting at 147°. It is decomposed by hot water with formation of *di-imidotriacetylmethylcyclopentene*, $CMe\begin{smallmatrix}CAc \cdot C:NH \\ CAc_2 \cdot C \cdot NH\end{smallmatrix}$, which forms colourless crystals melting at 194—198°. Dicyanacetylacetone is converted by ethylic acetoacetate, in presence of a small amount of sodium ethoxide, into *ethylic di-imidodiacetylmethylcyclopentenecarboxylate*, $C_{13}H_{16}N_2O_4$, which melts at 153—158°. Dicyanacetylacetone is, moreover, converted by alcohol containing a small amount of sodium ethoxide into a substance which forms well-developed, yellowish-green crystals melting at 162°, and is probably *di-imidodiacetyltrimethylene*, $CAc_2\begin{smallmatrix}C:NH \\ C:NH\end{smallmatrix}$. When cyanogen is passed into an alcoholic solution of ethylic malonate containing a small amount of sodium ethoxide, a red sodium salt, which has previously been described, separates, whilst the filtrate contains *ethylic dicyanomalonate* or *ethylic cyanimidoisosuccinate*, $NH:C(CN) \cdot CH(COOEt)_2$; this crystallises in colourless needles, and melts at 93°. A. H.

Derivatives of Ethylic Diethylacetoacetate. By Max Conrad and Richard Gast (*Ber.*, 1898, 31, 2954—2957).—*Ethylic γ-bromodiethylacetoacetate*, $CH_2Br \cdot CO \cdot CEt_2 \cdot COOEt$, obtained by treating ethylic diethylacetoacetate with the requisite quantity of bromine, is a colourless oil which boils at 245—255°, but at the same time undergoes partial decomposition, evolving hydrogen bromide. When boiled for some 15—20 hours with an alcoholic solution of potassium acetate, it yields the *acetate*, $OAc \cdot CH_2 \cdot CO \cdot CEt_2 \cdot COOEt$, boiling at 255—265° and having a sp. gr. = 1·058 at 15°/15°. When kept for 12 months, it decomposes into ethylic acetate and the *lactone* of *γ-hydroxydiethylacetoacetic acid*, $O\begin{smallmatrix}CH_2 \cdot CO \\ CO—CEt_2\end{smallmatrix}$, boiling at 219—225°.

The acetate mentioned above yields an oily *monobromo*-derivative, which, when boiled for several hours with baryta water, is converted into *β-diethylmalic acid*, $COOH \cdot CH(OH) \cdot CEt_2 \cdot COOH$, which melts at 117°.

β-Diethylethylidenelactic acid (*3-ethyl-2-pentanoloic acid*),
$$CHEt_2 \cdot CH(OH) \cdot COOH,$$
is obtained when the acetate is hydrolysed by boiling with dilute sulphuric acid for several days; it melts at 82° and yields a crystalline *silver* salt readily soluble in warm water. Just as ethylic dimethylacetoacetate, when treated with sodium, yields ethylic isobutyrate and ethylic sodio-γ-acetyldimethylacetoacetate (Abstr., 1898, i, 512), so ethylic diethylacetoacetate yields *ethylic sodio-γ-acetyldiethylacetoacetate*, $CH_3 \cdot C(ONa):CH \cdot CO \cdot CEt_2 \cdot COOEt$. This is best isolated in the form of its compound with mercuric chloride, namely,
$$CH_3 \cdot C(OHgCl):CH \cdot CO \cdot CEt_2 \cdot COOEt,$$
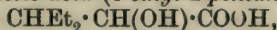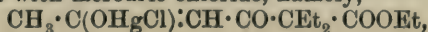
which can be recrystallised from ethylic acetate, and then melts at 152°. Free *ethylic γ-acetyldiethylacetoacetate* (ethylic 2 : 2-diethyl-3 : 5-hexanedionoate, or, according to Collie, ethylic α-diethyltriacetate) is obtained when the mercury derivative is treated with hydrogen sulphide and then extracted with ether ; it is a yellowish oil, has feebly acid properties, and, when shaken with copper acetate solution, yields a crystalline *copper* derivative, $(C_{12}H_{19}O_4)_2Cu$, which, after recrystallisation from light petroleum, melts at 82°.   J. J. S.

Tautomerism : Desmotropy of 2-Acetylangelicalactone. By LUDWIG KNORR and WILLIAM AUGUSTUS CASPARI (*Annalen*, 1898, **303**, 133—149).—On heating ethylic diacetosuccinate, ethylic iso-carbopyrotritarate, $COOEt \cdot C \diagdown \genfrac{}{}{0pt}{}{C(:CMe \cdot OH) \cdot CO}{CMe \underline{\quad\quad} O}$, is obtained (Abstr., 1894, i, 360). The authors find that when the free acid is distilled, carbonic anhydride is eliminated, and the two desmotropic 2-acetyl-angelicalactones produced ; these are distinguished as the α-lactone and the β-lactone respectively.

α-2-Acetylangelicalactone, $CH \diagdown \genfrac{}{}{0pt}{}{C(:CMe \cdot OH) \cdot CO}{CMe \underline{\quad\quad} O}$, the enolic form, is obtained in a highly purified condition on distilling the β-modification ; it crystallises from ether in long, colourless prisms, melts at 63°, and boils at 150°, 159°, and 216° under pressures of 45 mm., 100 mm., and 760 mm. respectively. It dissolves sparingly in water, which becomes acid. The lactone reduces ammoniacal silver nitrate and the chlorides of mercury and gold ; with alcoholic ferric chloride, it develops a characteristic cornflower-blue coloration which, after an interval, becomes violet, and, finally, red. Exposure to air causes the lactone to deliquesce, oxidation converting it into a yellow resin which dissolves readily in organic media and develops a deep red coloration with ferric chloride ; a certain amount of the β-modification is also produced. The *sodium* derivative is obtained by boiling a benzene solution of either isomeride with sodium wire in a reflux apparatus ; it is a colourless, amorphous powder, becoming reddish when exposed to air, and dissolves with extraordinary readiness in alcohol and in water. Dilute mineral acids precipitate the α-lactone from concentrated aqueous solutions of the sodium derivative, but carbonic anhydride yields chiefly the isomeride, which is precipitated exclusively from dilute solutions by this agent ; numerous metallic salts give rise to derivatives when added to moderately concentrated solutions of the sodium derivative. The *iron* derivative forms an indigo-blue, crystalline powder, and contains $4H_2O$; the *barium* derivative is crystalline, and also contains $4H_2O$. The *phenylurethane* melts at 102°. Concentrated sulphuric acid dissolves the α-lactone, and on pouring the liquid into water, pyrotritaric acid is produced. Diazomethane also acts on the lactone, forming a liquid which decomposes on distillation ; as the substance does not develop colour with ferric chloride, it is probably the methyl ether of the lactone.

β-2-Acetylangelicalactone, $CH \diagdown \genfrac{}{}{0pt}{}{CH(COMe) \cdot CO}{CMe \underline{\quad\quad} O}$, the ketonic form, crystallises from chloroform or glacial acetic acid in white leaflets and

melts indefinitely at 177—180°; at 20°, 1 part dissolves in 49·5 parts of chloroform, 121 parts of acetone, 296 parts of alcohol, 544 parts of benzene, or 3948 parts of ether. The β-lactone has reducing properties resembling those of the isomeride, but it does not develop colour with ferric chloride; it is indifferent to the action of air. The lactone dissolves slowly in dilute caustic soda, and yields a crystalline sodium derivative with the concentrated alkali; from freshly prepared solutions, mineral acids precipitate the unchanged substance, but if an interval has elapsed since the solution was formed, a certain amount of the α-lactone is obtained along with it, this being the exclusive product after the alkaline solution has been boiled. Concentrated sulphuric acid dissolves the lactone, and yields it unchanged if poured immediately into water, but if this operation is performed after an interval of 8 hours, pyrotritaric acid is obtained; protracted treatment with boiling water eliminates carbonic anhydride, and converts the lactone into acetonylacetone. Phenylic cyanate and diazomethane are without action on the β-lactone.

The conditions under which the two lactones are interconvertible are stated in the paper. In general, a low temperature favours the production of the ketonic modification. M. O. F.

Polyaspartic Acids. By HUGO SCHIFF (*Annalen*, 1898, **303**, 183—217. Compare Abstr., 1898, i, 67).—This paper contains experimental details relating to the former communication (*loc. cit.*). Whilst octaspartide combines with 8 mols. of phenylhydrazine, tetraspartide yields the *triphenylhydrazide*, $C_{34}H_{38}N_{10}O_9$, and the *tetraphenylhydrazide*, $C_{40}H_{46}N_{12}O_9$.

Octaspartide dissolves in aniline, forming anilides in which 3, 4, 6, or 8 aniline residues have combined with the corresponding number of carbonylic groups. Those derivatives in which fewer than 8 aspartide rings have been resolved are capable of further action with bases. Octaspartide *trianilide*, $C_{50}H_{47}N_{11}O_{17}$, is a greyish powder which becomes yellow at 90°, softens at about 245°, and decomposes as it melts. The *tetranilide*, $C_{56}H_{54}N_{12}O_{17}$, decomposes and evolves gas at 230—240°; it dissolves in phenylhydrazine, forming the tetraphenylhydrazide, $C_{80}H_{86}N_{20}O_{17}$, which becomes brown at about 190° and completely fused at 210°, when it decomposes. The *hexanilide*, $C_{68}H_{68}N_{14}O_{17}$, becomes brown at about 90°, and decomposes at 125°; the *octanilide*, $C_{80}H_{82}N_{16}O_{17}$, decomposes at about 130°.

Further action of boiling aniline converts the octaspartanilides into phenyloctaspartanilides, with elimination of ammonia. *Triphenyloctaspartoctanilide*, $C_{98}H_{94}N_{16}O_{17}$, *tetraphenyloctaspartoctanilide*, $C_{104}H_{98}N_{16}O_{17}$, and *pentaphenyloctaspartoctanilide*, $C_{110}H_{102}N_{16}O_{17}$, melt somewhat indefinitely at 120—125°, 170°, and 160° respectively.

Tetraspartide behaves towards aniline like octaspartide. The *dianilide*, $C_{28}H_{28}N_6O_9$, decomposes at 270—275° without undergoing fusion, whilst the *trianilide*, $C_{34}H_{35}N_7O_9$, melts indefinitely at 245—260°. The *tetranilide*, $C_{40}H_{42}N_8O_9$, softens at about 220°, and decomposes above 235°; the *phenyltetranilide*, $C_{46}H_{46}N_8O_9$, is a brownish-yellow powder which melts and decomposes at 130°.

The action of aniline on aspartic acid has also been investigated. M. O. F.

Conversion of Trimethylene into Propylene. By ALESEI A. WOLKOFF and BORIS N. MENSCHUTKIN (*Ber.*, 1898, **31**, 3067—3073. Compare Tanatar (Abstr., 1896, i, 457).—Pure trimethylene is best obtained by heating trimethylenic bromide (10 grams), zinc dust (12·5 grams), and 96 per cent. alcohol (20 c.c.) in a reflux apparatus at 70—80°, and passing the evolved gas through two wash-bottles containing bromine, then through sodium hydroxide solution and finally through a 0·5 per cent. solution of potassium permanganate, which should not become decolorised. It has been shown that trimethylene obtained by Gustavson's method always contains propylene, the amount varying between 13 and 39·5 per cent.; this can only be completely removed by passing the gas through bromine, when a small amount of the trimethylene is also absorbed. Tanatar's experiments have been repeated, pure trimethylene free from propylene being employed, and it has been found that when the purified gas is passed through a tube heated to dull redness, no trace of propylene is formed. A little oxymethylene is obtained, its formation being seemingly due to small amounts of air from the drying apparatus. Tanatar's results must be due to the fact that he employed trimethylene containing propylene. Experiments made at higher temperatures indicate that the products formed are ethylene, paraffin hydrocarbons, and hydrogen. Trimethylenic bromide is not converted into propylenic bromide by the action of zinc bromide, but yields *ethylic α-bromopropylic ether*, $CH_2Br \cdot CH_2 \cdot CH_2 \cdot OEt$, boiling at 147—148°, and having a sp. gr. $= 1·2597$ at 0°. This brom-ether, when treated with zinc-dust and alcohol, gives a nearly theoretical yield of propylene at 60—70°, together with a small quantity of ethylic allylic ether boiling at 67—72°. Allylic bromide, when treated in alcoholic solution with zinc dust, yields propylene. It seems probable then that the conversion of trimethylene into propylene is due to the following reactions. Trimethylenic bromide → ethylic α-bromopropylic ether → allylic ethylic ether → allylic bromide → propylene. J. J. S.

1 : 4-Dimethylhexamethylene. By NICOLAI D. ZELINSKY and S. NAUMOW (*Ber.*, 1898, **31**, 3206—3208).—Ethylic dimethylsuccinylosuccinate, when hydrolysed with dilute sulphuric acid, yields two stereoisomeric dimethyldiketohexamethylenes, the one, previously described by Baeyer (Abstr., 1892, 1183), melting at 93°, and a second crystallising from water in needles and melting at 115—117°. The mixture of the two ketones, when reduced according to Baeyer's method for the synthesis of quinitol (*ibid.*, 1833), yields a syrupy mass of dimethylquinitol, which, when further treated with 4—5 times its volume of concentrated hydrobromic acid at 100°, yields two stereoisomeric *dibromides*, the one an oil, and the other melting at 93—94°. The *di-iodide* of dimethylquinitol may be obtained in a similar manner, and when reduced by the zinc-palladium process (see this vol., i, 181) yields a hydrocarbon boiling at 118—119°. In the crude form, it has an aromatic odour, but this disappears on treatment with con-

centrated sulphuric acid. From its method of formation, this hydrocarbon must be 1 : 4-dimethylhexamethylene or hexahydroparaxylene. The boiling point found does not agree with that previously given by Schiff (Abstr., 1880, 892). When treated with bromine in the presence of aluminium bromide, Jacobsen's tetrabromoparaxylene is obtained. Hexahydroparaxylene differs but little in boiling point and specific gravity from the previously described hexahydrometaxylene.

<div style="text-align: right">J. J. S.</div>

Fluorine Derivatives of Toluene. By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1898, ii, 26—27; from *Bull. Acad. roy. Belg.*, [iii], **35**, 375—420).—When a mixture of benzotrichloride with two-thirds of its weight of antimony fluoride is heated quickly and boiled for 5 minutes, *ω-difluorochlorotoluene*, $CPhFCl_2$, and *ω-trifluorotoluene*, $CPhF_3$, are obtained. The former is a colourless liquid, boils at 142·6° under a pressure of 770 mm., has a sp. gr. = 1·25445 at 13°, and a specific refractive index = 1·46969; the latter is a colourless liquid, boils at 103·5°, has a sp. gr. = 1·19632 at 14°, and a specific refractive index = 1·41707. Trifluorotoluene is not decomposed at high temperatures, and not attacked by water, alkalis, phenols, aniline, reduced copper, or phenylhydrazine; with fuming nitric acid, it yields *ω-trifluorometanitrotoluene*, $NO_2 \cdot C_6H_4 \cdot CF_3$, which boils at 201·5°, has a sp. gr. = 1·43571 at 15°, and a specific refractive index = 1·47582; this is reduced by stannous chloride and hydrochloric acid to *ω-trifluorometatoluidine*, which boils at 187·5°, has a sp. gr. = 1·30467 at 12·5°, and a specific refractive index = 1·4847; the *hydrochloride* and *nitrate* were prepared. By the action of acetic anhydride on trifluorotoluidine, *acetotrifluorotoluidide* is obtained; it crystallises from water in needles, melts at 103°, and boils at 287°. *Trifluorometatoluonitrile*, $CF_3 \cdot C_6H_4 \cdot CN$, prepared by means of the diazo-compound, melts at 14·5°, boils at 189°, has a sp. gr. = 1·28126 at 20°, a specific refractive index = 1·45048, and when hydrolysed yields isophthalic acid and *trifluorometatoluic acid*, $CF_3 \cdot C_6H_4 \cdot COOH$; the latter crystallises from chloroform in needles, melts at 103°, boils at 238·3° under a pressure of 770 mm., and yields crystalline *sodium*, *silver*, *lead*, and *barium* salts. The physical constants of the above fluorine derivatives were determined.

<div style="text-align: right">E. W. W.</div>

Influence of Light on Chemical Substitution. By CORNELIUS RADZIEWANOWSKI and JULIAN SCHRAMM (*Chem. Centr.*, 1898, i, 1019—1020; from *Akad. Wiss. Krakau*, 1898, Februarheft, 61—68).—By the action of chlorine (1 mol.) on ortho-xylene (1 mol.) in sunlight, *ortho-xylylic* and *ortho-xylylenic chlorides* are formed; the former boils at 195—203°, the latter crystallises in long prisms, melts at 55°, boils at 240—260°, and constitutes the main portion of the product when twice the above quantity of chlorine is used. The fractions of higher boiling point yield *ortho-xylene hexachloride*, $C_6H_4Me_2Cl_6$, which forms rhombic crystals, melts at 194·5°, and boils at 260—265°; it is soluble in benzene, chloroform, and carbon bisulphide, but insoluble in alcohol and ether. By the action of chlorine on paraxylene in sunlight, *paraxylylic* and *paraxylyl-*

enic chlorides are obtained ; the former boils at 200—202°, the latter crystallises in rhombic plates and melts at 100°. Metaxylene yields a mixture of metaxylylic chloride and chlorometaxylene with some *metaxylylenic chloride.* Substances containing more side chains in the meta-position are apparently not so susceptible to the influence of light as regards the action of chlorine, for chlorine and bromine do not attack mesitylene as readily as metaxylene. In the product obtained by the action of chlorine (2 mols.) on ethylbenzene in sunlight, *dichlorethylbenzene*, CCl_2MePh, was detected by the formation of acetophenone when heated with silver oxide ; substitution also occurs to some extent in the benzene ring. E. W. W.

Action of Mercuric Chloride on Aqueous Phenol Solutions. By BRUNO GRÜTZNER (*Arch. Pharm.*, 1898, **236**, 622—626).—When a saturated solution of mercuric chloride in a 5 per cent. aqueous solution of phenol is heated to boiling and then allowed to cool, *hydroxyphenylmercury chloride*, $OH \cdot C_6H_4 \cdot HgCl$, separates in mossy crystals, soluble with difficulty in alcohol, and almost insoluble in benzene, chloroform, and light petroleum.

The author has, however, abandoned the investigation of this substance, owing to Dimroth's work (this vol., i, 54) in the same direction. A. W. C.

Constitution and Cryoscopic Behaviour of Orthocyanophenols. By KARL AUWERS and A. J. WALKER (*Ber.*, 1898, **31**, 3037—3045).—It has been shown that phenols containing a negative substituent in the ortho-position relatively to the hydroxyl group exhibit normal cryoscopic behaviour, that of the corresponding meta- and para-compounds being abnormal (compare Abstr., 1896, ii, 293) ; orthocyanophenol is the only exception which has been hitherto observed, and the desmotropic formula, $C_6H_4 < {}^{O}_{C:NH}$, was suggested by Victor Meyer to account for the peculiarity. The authors consider, however, that the chemical and cryoscopic behaviour of the substance is incompatible with this supposition, and the abnormal value of the molecular weight remains unexplained.

The *ammonium* derivative of orthocyanophenol melts at 139—141°, evolving ammonia ; the *silver* derivative becomes dark under the influence of light. The *benzylic ether*, whether prepared from the silver derivative and benzylic iodide in benzene, or from the sodium derivative and benzylic chloride in alcohol, crystallises from petroleum in white needles, and melts at 71—72°. The *oxime* of benzylsalicylaldehyde crystallises from petroleum in white leaflets, and melts at 71·5° ; boiling acetic anhydride converts it into the benzylic ether of orthocyanophenol.

The *benzylic ether* of paracyanophenol separates from petroleum in white needles, and melts at 94—94·5°.

The *oxime* of the benzylic ether of parahydroxybenzaldehyde melts at 110—111·5°, and yields the benzylic ether of paracyanophenol under the influence of boiling acetic anhydride.

Bromocyanophenol [OH : CN : Br = 1 : 2 : 4], prepared from the oxime

of bromosalicylaldehyde, crystallises from benzene or dilute alcohol, and melts at 158—159°. *Dibromocyanophenol* [OH:CN:Br$_2$ = 1:2:4:6], produced by the direct action of bromine on orthocyanophenol, crystallises from a mixture of benzene and petroleum in silky needles, and melts at 167—168°; prisms melting at the same temperature are obtained by using alcohol or benzene, but a mixture of the two forms melts at 163°.

Nitrosalicylonitrile and dinitrosalicylonitrile have been prepared by Victor Meyer and Bone. *Bromonitrosalicylonitrile* [OH:CN:Br:NO$_2$ = 1 : 2 : 4 : 6], produced by the action of fuming nitric acid on bromosalicylonitrile, crystallises from petroleum in yellow needles, and melts at 119—120°. *Nitrosalicylonitrile* [OH : CN : NO$_2$ = 1 : 2 : 3] crystallises from boiling water in yellow leaflets, and melts at 207—208°.

The cryoscopic behaviour of the foregoing bromo- and nitro-compounds, and of the benzylic ether of salicylonitrile has been examined in naphthalene. The results are normal in the case of dibromocyanophenol, dinitrocyanophenol, and bromonitrocyanophenol, abnormal in the case of bromocyanophenol; nitrocyanophenol [OH : CN : NO$_2$ = 1 : 2 : 4] is sparingly soluble in naphthalene, whilst the isomeride, [OH : CN : NO$_2$ = 1 : 2 : 3], is probably abnormal. M. O. F.

Phenol-quinones and -quinhydrones. Mixed Phenol-quinones. By ALFRED BILTRIS (*Chem. Centr.*, 1898, i, 887—888; from *Bull. Acad. roy. Belg.*, [iii], **35**, 44—67).—When boiling solutions of absolutely pure paracresol (2 mols.) and quinone (1 mol.) in light petroleum are mixed, the liquid quickly becomes red, and *paracresol-quinone*, C$_6$H$_4$O$_2$,2C$_6$H$_4$Me·OH, soon crystallises out in red needles; it can be recrystallised from boiling ether, melts at 62°, sublimes without decomposing, and is soluble in ether, benzene, and hot light petroleum. *Orthocresol-quinone*, prepared in a similar way, crystallises in red needles and melts at 64°. Metacresol does not act on quinone. *Paracresol-phenol-quinone*, C$_6$H$_4$O$_2$,PhOH,C$_6$H$_4$Me·OH, obtained by mixing ethereal solutions of quinone, phenol, and cresol, and evaporating the ether, crystallises in reddish-brown needles, melts at 48°, decomposes spontaneously, and is soluble in benzene, ether, and hot light petroleum; *cresol-phenol-quinone* crystallises in reddish-brown needles and melts at 67°. *Thymol-phenol-quinone*, C$_6$H$_4$O$_2$,PhOH,C$_6$H$_3$MePr·OH, prepared by mixing solutions of quinone, thymol, and phenol in ether and evaporating, crystallises in red needles, which, after about 2 days, change into small, blackish crystals; it melts at about 127°. When ethereal solutions of phenol (2 mols.) and toluquinone (1 mol.) are mixed and evaporated, *phenol-toluquinone*, C$_6$H$_3$O$_2$Me,2PhOH, is obtained as a red syrup, which solidifies when immersed in a freezing mixture; it melts at 18°. *Phenol-thymoquinone*, C$_6$H$_2$MePrO$_2$,2PhOH, prepared in like manner, is a red syrup which solidifies below 0°.

When lukewarm aqueous solutions of thymoquinol and ordinary quinone are mixed, thymoquinone instantly separates, and quinol with small quantities of the mixed quinhydrone remain in the mother liquor.

Determinations of the freezing points and boiling points of solutions of several quinhydrones and phenol-quinones show that both classes

of compounds are decomposed even in saturated solution in neutral solvents, and thus behave like additive compounds; this behaviour is also explained by Jackson and Oenslager's formula, in which a hemi-acetal constitution is assumed.   E. W. W.

Halogen Derivatives of Guaiacol and Veratrole. By H. COUSIN (*Compt. rend.*, 1898, **127**, 759—760).—*Trichloroguaiacol*, obtained by the action of chlorine on a chloroform solution of guaiacol, crystallises from alcohol in white needles and melts at 114—115°. The tetra-chloro-derivative is not obtained by the prolonged action of chlorine. *Trichloroveratrole*, prepared by the action of methylic iodide on trichloro-catechol, or on the preceding compound, crystallises in white, prismatic needles and melts at 68—69°; it is somewhat insoluble in alcohol, but dissolves readily in benzene. *Dibromoguaiacol*, produced by direct bromination of guaiacol in cold chloroform solution, forms white, flattened, prismatic needles readily soluble in alcohol. *Tetrabromo-guaiacol*, obtained by adding excess of bromine to guaiacol dissolved in concentrated sulphuric acid, crystallises from hot alcohol in clusters of prisms and melts at 160°. *Tribromoveratrole* results from the action of methylic iodide and alcoholic potash on tribromoguaiacol; it crystal-lises from alcohol in prismatic, silky needles, and melts at 83—84°.
                                                            G. T. M.

Behaviour of Certain Groups of Cyclic Compounds towards Metallic Sodium. By HERMANN KUNZ-KRAUSE (*Arch. Pharm.*, 1898, **236**, 542—570. Compare Abstr., 1898, i, 479).—The action of metallic sodium on chrysatropic acid in alcoholic solution has already been studied by the author, who now applies the reaction to a variety of substances, in order to find out how far the fluorescence, produced in some cases, is connected with the constitution of the compound. Among other conclusions, it is held that the reaction gives valuable information as to the constitution of certain tannin substances.

Phenol, thymol, anisol, phenetoil, resorcinol dimethylic ether, anethoil, menthol, camphor, and caryophyllin, when treated with sodium in ethylic alcohol solution, do not give characteristic colour reactions. Catechol is turned green, then deep blue stripes appear on the glass, and a dark-green precipitate forms; resorcinol, blue-yellow to olive-green coloration; quinol, orange-yellow to brown coloration, and formation of an olive-green precipitate; orcinol, blood-red coloration, and flesh-coloured crusts form on the sodium, which, on standing, are changed into glistening, six-sided, rhombic prisms of the formula $C_6H_3Me(ONa)_2 + H_2O$. With pyrogallol, deep blue crusts are formed. α-Naphthol gives a greenish-blue fluorescence; β-naphthol, a bluish-violet fluorescence, changing to olive, brown, and then orange; guaiacol, a yellow coloration, changing to green and then black; eugenol, an intense yellow coloration, and santonin an orange-red.

Salicylic acid gives a rose coloration changing to grey-green, with deposition of a grey, crystalline precipitate; protocatechuic acid, blue coloured crusts, dissolving in water to a yellowish-brown solution; gallic acid, blue crusts, or a blue solution changing to brownish-black, and formation of a colourless, crystalline precipitate, and tannin, bluish-green crusts, with production of a colourless, crystalline mass.

Orthomethoxycoumaraldehyde gives a yellow colour; cinnamic acid, microscopic, glistening needles of the composition $CHPhNa\cdot CHNa\cdot COONa$; 3 : 4-dihydroxycinnamic acid, an intense dark-green coloration, and the yellow alcoholic solution of piperic acid is decolorised, and a white precipitate is formed.

From the behaviour of the various hydroxy-derivatives of coumarin, it appears that the fluorescence is intensified by the presence of side-chains in the benzene ring, but there is no direct relation between the intensity of the fluorescence and the number of entering hydroxy- or methoxy-groups. The author thinks it probable that fluorescence is due to the presence of the groups OH and $CH\vdots CH\cdot COOH$ in the ortho position, caused by the splitting of the lactone ring.

In order to study the influence exerted on the fluorescence by the removal of the carboxyl group, *orthovinylphenol*, $OH\cdot C_6H_4\cdot CH\vdots CH_2$, was prepared by heating orthocoumaric acid; it is a yellow to greenish-brown oil, solidifying, on standing, to a brittle, glassy mass. Its alkaline solution is non-fluorescent, thus affording a definite proof of the fact that the fluorescence of orthocoumaric acid depends on the presence of the carboxyl group.

As the fluorescence of the above-mentioned substances is particularly noticeable in alkaline solution, the behaviour of organic bases was tried in this direction. A solution of chrysatropic acid (4-hydroxy-5-methoxycoumarol) in aniline is colourless, whilst in pyridine an intense yellow colour is produced. Both solutions are non-fluorescent. At the same time, beautifully crystalline, molecular compounds of the two substances are formed, and, as their solutions are highly refractive, the author proposes to prepare a number of these compounds, more particularly to study the influence of the various side-chains on the refractive properties of their solutions.

The sodium reaction has also been tried on the following tannin substances.

Glycosyl-dihydroxycinnamic acid gives an intense yellow coloration, and a golden-yellow precipitate of a sodium compound, dissolving in water to form a yellow solution, gradually changing to green and then brown; Fabianaglycotannin, from *Fabiana imbricata*, a similar behaviour to the above, but the colour of the aqueous solution of the sodium compound is a permanent yellow; Rochleder's boheic acid and tannin, from *Sorbus aucuparia*, intense yellow precipitates; maclurin, a yellow colour and precipitate; and catechin, a flesh-coloured precipitate changing to a brown resin.

Among the alkaloids, piperine gives an intense yellow colour, but no precipitate, when treated with sodium in alcoholic solution.

A. W. C.

Formation of Chains. XXXI. Dimethylaniline and Ethereal Salts of α-Bromo-acids. By CARL A. BISCHOFF (*Ber.*, 1898, **31**, 3015—3025).—Weinig has stated (Abstr., 1895, i, 17) that diethylaniline is a satisfactory agent for converting ethylic α-bromisovalerate into ethylic dimethylacrylate, whilst dimethylaniline is unsuitable. The author finds that the latter base yields trimethylphenylammonium bromide with ethylic α-bromopropionate, giving rise to unsaturated

salts with ethylic α-bromisobutyrate and ethylic α-bromisovalerate ; ethylic α-bromobutyrate, however, remains practically indifferent towards the base, illustrating the dissimilarity between the propionic and butyric radicles anticipated by the collision hypothesis.

[With TARASCHTSCHANSKY.]—*Trimethylphenylammonium bromide*, $C_9H_{14}BrN$, prepared from methylic bromide and dimethylaniline, is identical with the salt obtained from ethylic α-bromopropionate and the base ; it decomposes at 203—204°. Ethylic methylanilidopropionate, NMePh·CHMe·COOEt, the bye-product in the latter method of preparation, is identical with the salt obtained from ethylic bromopropionate and methylaniline (Abstr., 1898, i, 183) ; hydrolysis converts it into *methylphenylalanine*, NMePh·CHMe·COOH, a viscous oil.

[With GRÜNBERG.]—Attempts to prepare ethylic methylanilidobutyrate (*loc. cit.*) from dimethylaniline and ethylic α-bromobutyrate were unsuccessful.

[With BRODSKY.]—A polymeride of ethylic methylacrylate was obtained from dimethylaniline and ethylic α-bromisobutyrate.

[With CARL BERNHARD.]—Ethylic dimethylacrylate was produced on heating ethylic α-bromisovalerate with dimethylaniline during 6 hours ; it is possible that a small quantity of ethylic α-methylanilidoisovalerate was formed along with it.   M. O. F.

Formation of Chains. XXXII. Comparison of Aromatic Bases in their Behaviour towards Ethereal Salts of α-Bromoacids. By CARL A. BISCHOFF (*Ber.*, 1898, **31**, 3025—3033).—A discussion and summary of the author's investigation of the influence exerted by the group a, b, X, Y, on the course of the change represented by the equation $2NHXY + COOEt·CabBr = NH_2XYBr + COOEt·Cab·NXY$.   M. O. F.

Action of Ammonium Sulphide on Nitrated Aromatic Nitramines and Nitrosamines. By JOHANNES PINNOW and PAUL R. OESTERREICH (*Ber.*, 1898, **31**, 2926—2934. Compare Abstr., 1897, i, 338).—Paranitrophenylmethylnitramine is converted by ammonium sulphide in alcoholic solution into paranitromethylaniline, melting at 152°. Orthonitrophenylmethylnitramine may be prepared by the methylation of orthophenylnitramine, and is converted by alcoholic ammonium sulphide into orthonitromethylaniline melting at 36°. Orthonitroparatolylmethylnitramine is reduced by ammonium sulphide to *amidotolylmethylnitramine* (*paramethylnitramido-orthotoluidine*,

$$[Me : NH_2 : N = 1 : 2 : 4]),$$

which crystallises in thin, dull red prisms melting at 83·5°. Paranitrophenylmethylnitrosamine is converted by ammonium sulphide into paranitromethylaniline, whilst orthonitroparatolylmethylnitrosamine yields the corresponding *amido*-compound (*methylnitrosamidotoluidine*), which crystallises in slender, sulphur-yellow needles melting at 83°. The *hydrochloride* is very unstable, but the *picrate* is more stable, and melts at 103—105°. This base readily undergoes the diazo-reaction, yielding a salt which reacts with β-naphthylamine to form *methylnitrosamido-orthotolueneazo-β-naphthylamine*, $C_{18}H_{17}N_5O$;

this crystallises in fiery red, slender needles melting at 179°. *Para-methylnitrosamido-orthoacetotoluidide*, prepared from the base by the action of acetic anhydride in ethereal solution, crystallises in yellowish prisms melting at 142°; the *thiocarbamide* of the base melts at 158°.

α-Metaxylidine is converted by methylic alcohol at 170—180° into *methylxylidine*, which is an oil boiling at 220·5—221·5°; the corresponding *nitrosamine* is an uncrystallisable oil. *Acetomethylxylide* crystallises in slender, white needles or compact prisms melting at 65°. Xylylmethylnitrosamine is converted by nitric acid into a *nitro-compound* which forms a heavy, almost white, crystalline powder melting at 63°, and has the constitution $[\mathrm{Me} : \mathrm{N_2} : \mathrm{NO_2} = 1 : 3 : 4 : 5]$; when heated with hydrochloric acid and aniline in alcoholic solution, it yields *nitromethylxylidine*, which melts at 58° and crystallises in long, carmine-red plates with a green reflex. This compound, by reduction with tin and hydrochloric acid, is converted into *methylxylylenediamine*, $\mathrm{C_9H_{14}N_2}$, which boils at 260—262° and yields a crystalline *hydrochloride* melting at 225°. Nitrous acid converts this substance almost quantitatively into *methylazimidoxylene*, $\mathrm{C_9H_{11}N_3}$, which crystallises in nodular aggregates of almost colourless needles melting at 118·5—119°; this reaction shows that the two amido-groups are in the ortho-position. *Diacetylmethylxylylenediamine* crystallises in broad needles melting at 195—196°. Nitroxylylmethylnitrosamine is reduced by ammonium sulphide to *amidoxylylmethylnitrosamine*, which crystallises in lustrous plates melting at 81°; the *picrate* melts at 128°. *Methylnitrosamido-symmetrical-xyleneazo-β-naphthylamine*, prepared in the usual manner, crystallises in long, lustrous, red plates melting at 184°. *Acetamidoxylylmethylnitrosamine* crystallises in thin, white plates melting at 135°. *Methylnitrosamido-xylylphenyl-thiocarbamide* forms thick prisms and melts at 132—132·5°.

A. H.

Nitrations with Nitrous Acid. By JOHANNES PINNOW (*Ber.*, 1898, **31**, 2982—2987).—It has been shown in several cases (Abstr., 1898, i, 134, &c.) that when a para-substituted dialkylaniline is nitrated by means of nitrous acid, the nitro-group takes the ortho-position relatively to the alkylamido-group. The formation of the substance described by Koch (Abstr., 1887, 1041) as metanitropara-chlorodimethylaniline appeared, therefore, anomalous; it is shown, however, that this substance is really an ortho-compound $[\mathrm{NMe_2} : \mathrm{NO_2} : \mathrm{Cl} = 1 : 2 : 4]$, for when it is reduced with tin and hydrochloric acid and the product fractionated, a base is obtained (4-*chloro-2-amidodimethyl-aniline*; boils at 266·5—267·5° under a pressure of 751 mm.; the yellow *picrate* melts at 190—191°), which, when heated with acetic anhydride at 145—160°, yields N-α-*dimethyl-2-chlorobenzimidazole*, $\mathrm{C_6H_3Cl} {\color{black}\overset{\displaystyle\diagup \mathrm{N} \diagdown}{\underset{\diagdown \mathrm{NMe} \diagup}{}}} \mathrm{CMe}$, melting at 130—131°, whilst its *mercurochloride* melts at 277—278°; moreover, the higher boiling fraction obtained in the reduction yields the *mercurochloride*, melting at 243—244°, of N-*methyl-2-chlorobenzimidazole*, $2\mathrm{C_6H_3Cl} {\color{black}\overset{\displaystyle\diagup \mathrm{N} \diagdown}{\underset{\diagdown \mathrm{NMe} \diagup}{}}} \mathrm{CH,H_2HgCl}$ (compare Abstr., 1898, i, 182).

When 4-chlorodimethylaniline is dissolved in dilute sulphuric acid and nitrated with dilute nitric acid, the product is a yellowish-red 4-*chlorodinitrodimethylaniline* $[(NO_2)_2 = 2 : 6$ (?)], which melts at 111—112°. When it is nitrated at $-10°$ with strong sulphuric acid and nitric acid of sp. gr. = 1·4, 4-*chloro-3-nitrodimethylaniline* is the product; this is yellow, and melts at 81·5—82·5°.

It would seem that nitrous acid is incapable of effecting nitration when the ortho-position relatively to the dimethylamido-group is already occupied.   C. F. B.

Derivatives obtained by the Action of Carbon Bisulphide on Dimethylaniline. By JOH. WEINMANN (*Chem. Centr.*, 1898, i, 1028—1029; from *Bull. Soc. ind. Mulhouse*, 1898, 40—43).—Carbon bisulphide alone does not act on dimethylaniline even at high temperatures, but in presence of metallic salts, such as zinc chloride, the following compounds are obtained. *Dimethylamidothiobenzoic acid* is prepared by shaking a mixture of 4 kilograms of carbon bisulphide, 30—40 kilograms of dimethylaniline, and 20 kilograms of zinc chloride for about 100 hours at 60—70°. The zinc chloride is removed by shaking with water containing acetic acid, the thio-acid being extracted with sodium hydroxide solution and precipitated with hydrochloric acid. *Tetramethyldiamidodiphenyl thioketone* is prepared by keeping the above mixture at 80° for 100—120 hours, removing the unchanged thio-acid, filtering off the zinc sulphide, removing the excess of dimethylaniline by distillation with steam, and finally treating the residual thioketone with very dilute hydrochloric acid to remove hexamethylparaleucaniline. The thioketone crystallises from carbon bisulphide in large crystals with a lustre like that of iodine, and, when heated with alcoholic ammonia under pressure, yields auramine, whilst with alcoholic aqueous ammonia it forms Michler's ketone. Hexamethylparaleucaniline is obtained by heating the mixture of carbon bisulphide, dimethylaniline, and zinc chloride at 100°. *Tetramethylthioaniline* is prepared by keeping the above mixture for several hours at 130—140°. After removing the thio-acid and dimethylaniline, the thio-base is separated from the diphenylmethane base, $CH_2(C_6H_4 \cdot NMe_2)_2$, which is also formed by fractional crystallisation from alcohol, or by precipitating the solution of the hydrochloride with excess of hydrochloric acid. Tetramethylthioaniline crystallises in lemon-coloured prisms, and melts at 178° (uncorr.); the hydrochloride, which forms colourless leaflets, gradually becoming yellow when exposed to the air, is decomposed by water. The sulphur is possibly in the para-position relatively to the dimethylamido-group, for in Tursini's isomeric base which melts at 125°, these groups occupy relatively the ortho-position.
                                          E. W. W.

Tertiary Aromatic Amines. I. By CARL HAEUSSERMANN and EUGEN BAUER (*Ber.*, 1898, **31**, 2987—2989).—Triphenylamine, when treated in acetic acid solution at the ordinary temperature with sodium nitrite, yields nitrotriphenylamine (Herz, Abstr., 1890, 1409).

Diphenylorthotoluidine, $NPh_2 \cdot C_6H_4Me$, was obtained by dissolving potassium (1 part) in diphenylamine (15 parts), heating the solution to 240—245°, and adding orthochlorotoluene (3·5 parts) gradually;

after 2—3 hours the product was allowed to cool and extracted with ether; from the extract, the ether was first distilled off, and then the excess of chlorobenzene and diphenylamine under reduced pressure; the residue was dissolved in light petroleum, any diphenylamine still present was precipitated as the hydrochloride by passing in gaseous hydrogen chloride, and the residue was freed from hydrogen chloride and petroleum, and then distilled under a pressure of 60 mm., when the fraction that boiled above 275° was found to solidify in part after several months; the crystals melted at 69—70°. When diphenylorthotoluidine is dissolved in acetic acid and treated with sodium nitrite, a yellow *mononitro*-derivative, melting at 164—165°, is obtained; if nitric acid is added instead of sodium nitrite, no such derivative is formed. C. F. B.

Combination of Phenylhydrazine with Metallic Salts. By PASTUREAU (*Compt. rend.*, 1898, **127**, 485—486).—When 5 grams of melted phenylhydrazine is added gradually to a boiling solution of 10 grams of bismuth chloride in 100 c.c. of dilute hydrochloric acid, and the liquid is evaporated at a gentle heat to about one-third of its bulk and allowed to cool, the compound $BiCl_3,6N_2H_3Ph$ separates in masses of colourless needles; it dissolves in dilute acids, and the solutions give all the reactions of the bismuth salt and phenylhydrazine. The compound $Bi3NO_3,6N_2H_3Ph$ is obtained in colourless, prismatic needles in a similar manner, but the temperature must not at any stage exceed 60°, or oxidation will take place. Its solution likewise gives all the reactions of the bismuth salt and phenylhydrazine. The compound $ZnSO_3,2N_2H_3Ph$ is obtained in colourless needles by dissolving 10 grams of zinc chloride in 100 c.c. of dilute acid, adding 50 c.c. of the ordinary solution of sodium hydrogen sulphite, and 5 grams of phenylhydrazine. A manganese compound, $MnSO_3,2N_2H_3Ph$, is obtained in a similar way. C. H. B.

Compounds of Phenylhydrazine with Haloid Salts of the Alkaline Earth Metals. By JOSEPH MOITESSIER (*Compt. rend.*, 1898, **127**, 722—723).—The *compound* $CaCl_2,2N_2H_3Ph$, obtained by adding phenylhydrazine to an alcoholic solution of calcium chloride, crystallises from hot alcohol in rhombic plates and readily dissolves in water, but is insoluble in ether. The strontium compound is unstable. The *compound* $CaBr_2,4N_2H_3Ph + 3H_2O$, which crystallises in long needles when phenylhydrazine is added to an aqueous solution of calcium bromide, is soluble in alcohol, but not in ether; when boiled with benzene, the whole of the aromatic base is eliminated. The *compound* $SrI_2,4N_2H_3Ph$ is obtained in prismatic crystals from an alcoholic solution of its components; it is deliquescent and decomposes at 100°. The corresponding *compound* from strontium bromide is also deliquescent; it is decomposed by dry ether. Phenylhydrazine combines with the fluorides of the zinc group, but not with those of calcium or strontium; it forms analogous compounds with lithium bromide and with the benzoates and oxalates of the zinc group.

G. T. M.

Action of Phenylhydrazine on Chloranilic Acid. By A. DESCOMPS (*Compt. rend.*, 1898, **127**, 665—666).—On adding chloranilic

acid (1 mol.) dissolved in alcohol, drop by drop, to an alcoholic solution of phenylhydrazine (3 mols.), the compound $C_6Cl_2O_2(OH)_2,2N_2H_3Ph$ separates on standing in slender, brownish-violet crystals; this action corresponds with that of phenylhydrazine on phloroglucinol (Baeyer and Kochendoerfer, Abstr., 1889, 1162), and on quinol and orcinol (Seyewitz, Abstr., 1892, 49).   W. A. D.

Isomeric Benzoylacetoximes. By JULIUS SCHMIDT (*Ber.*, 1898, **31**, 3225—3229).—When sodium wire (4·6 grams) is gradually covered with a solution of acetoxime (14·6 grams) in perfectly dry ether, the re-action is at first violent, but slackens and requires some four days before it is completed; the sodium salt is well washed with dry ether, then suspended in ether, and treated with rather less than the theoretical quantity of benzoic chloride. The oil which is left after distilling off the ether partially solidifies, and is a mixture of a liquid benzoyl-acetoxime with the solid one already described by Janny (Abstr., 1883, 581); these may be separated by the aid of a suction pump. Janny's compound, $CMe_2:N\cdot O\cdot COPh$, is readily soluble in alcohol, ether, chloroform, or benzene, sparingly in light petroleum, melts at 43—44° (Janny gives 41—42°), and is slowly hydrolysed by dilute sodium hydroxide, but is not acted on by 1 per cent. solution of sodium carbonate; it is soluble in cold fuming hydrochloric acid, but after a few hours benzoic acid is deposited, and under certain circumstances a compound melting at 30—32°, and probably α-benzoylhydroxylamine,

is formed. The liquid isomeride, $C{<}^{N\cdot COPh}_{CMe_2}$, is a pale yellow, mobile,

oil of sp. gr. = 1·0981 at 14°/4° and refractive index $n_D = 1.5279$ at 14°, miscible in all proportions with alcohol, ether, chloroform, or benzene. One hundred parts of light petroleum (b. p. 50—60°) dissolve, at 20°, 6·58 parts of the oil. Its alcoholic solution, when treated with ferric chloride, gives an intense red-violet coloration. It is slowly transformed at the atmospheric temperature into Janny's compound, more quickly when treated with alkalis.   J. J. S.

Benzoate of Acetohydroxamic Acid. By FRANK K. CAMERON (*J. Physical Chem.*, 1898, **2**, 376—381).—The benzoate of acetohydroxamic acid (Jones, Abstr., 1898, i, 172) has a melting point of 99°, but on precipitating the compound from its solution in ether by the addition of light petroleum, an isomeric modification melting at 70° is obtained. The author calls the first the α-, and the second the β-compound. Both modifications exist in the liquid phase. The α-modification is the stable one at the ordinary temperature. Crystals of the β-modification can be obtained by dissolving the α-compound and precipitating suddenly from solution; the α-modification is converted into the β-modification with absorption of heat. By raising the tem-perature of the system and cooling rapidly, the point of solidification may be brought below the stable triple point. It is not possible to realise the eutectic point in this manner, as the compound decomposes; the eutectic point is near 65°. The temperature of the stable triple point is about 95°.   H. C.

Modification of Friedel and Craft's Method of Synthesis by aid of Aluminium Chloride. By A. VERLEY (*Bull. Soc. Chim.*, 1897, [iii], 17, 906—914).—In order to eliminate the hydrogen chloride formed in the action and to prevent the formation of resinous substances, the author carries out the condensation at 0° and in a vacuum, the acid or alkylic chloride being added drop by drop to a cooled mixture of the hydrocarbon with aluminium chloride; the yield is good, and the method is especially advantageous in the preparation of ketones. Thus, by the action of acetic chloride on the corresponding hydrocarbons, the author has obtained yields of 80 per cent. of paratolyl methyl ketone, metaxylyl methyl ketone [Me : Me : Ac = 1 : 3 : 4], and paracymyl methyl ketone [Me : Ac : Pr^β = 1 : 2 : 4]; he contradicts the statement of Essner and Gossin (Abstr., 1885, 252), that metatolyl methyl ketone is produced by this method. *Paratolyl bromomethyl ketone,* melting at 51°, and *paratolyl dibromomethyl ketone,* melting at 99°, are produced by the action of one and of two molecules of bromine on paratolyl methyl ketone; the monobromo-derivative is readily oxidised by alkaline potassium permanganate to paratolylglyoxylic acid, $C_6H_4Me\cdot CO\cdot COOH$, which, when heated with aniline, loses carbonic anhydride and gives the corresponding aldehyde. This is a general method for preparing aromatic aldehydes, and from cymene the author has thus obtained *methylisopropylbenzaldehyde,* [Me : CHO : Pr^β = 1 : 2 : 4]; this boils at 132° under a pressure of 20 mm., or at 238° under 760 mm. pressure; and has a sp. gr. = 0·9988 at 0°. It has an unpleasant odour recalling that of carrots, and in presence of a trace of sodium condenses with acetone to form the compound $C_3H_7\cdot C_6H_3Me\cdot CH{:}CH\cdot CO\cdot CH_3$, which has the characteristic odour of saffron.

The first product of the action of ethylic chloroglyoxylate on paracymene is *ethylic cymylglyoxalate,*

$$C_6H_3MePr^\beta\cdot CO\cdot COOEt \quad [Me : C_2O_3Et : Pr^\beta = 1 : 2 : 4],$$

of which, however, only a 20 per cent. yield could be obtained; this boils at 130—132° under a pressure of 21 mm., or under atmospheric pressure at 237° with decomposition; its sp. gr. = 0·9841; it has a disagreeable odour, which, when diluted, is somewhat suggestive of violets; by the further action of aluminium chloride, it loses carbonic oxide and anhydride, and is converted into ethylcymene [Me : Et : Pr^β = 1 : 2 : 4]. When chloromethylic ethylic ether is added to a mixture of benzene and aluminium chloride, it gives a theoretical yield of diphenylmethane, and can, therefore, be used with advantage in place of methylenic chloride for the preparation of this substance; the first product of the action is probably benzylic ethylic ether, which, in presence of hydrogen chloride, is converted into benzylic chloride, and then condenses with a second molecule of benzene. T. M. L.

Chlorophosphine of Orthochlorotoluene. By P. MELCHIKER (*Ber.*, 1898, 31, 2915—2919).— 2-*Chlorotolyl-4-chlorophosphine,* $C_6H_3MeCl\cdot PCl_2$, can be obtained from 2-chlorotoluene (compare Abstr., 1897, i, 146), but the yield is small; it boils at 265—266°, and has a sp. gr. = 1·373 at 22°. When decomposed with water, it forms the

phosphinous acid, $C_6H_3MeCl\cdot P(OH)_2$; this melts at 70°; its yellow
phenylhydrazine salt at 156·5°; the anhydrous *ammonium* and *barium*
salts were also analysed. The *tetrachloride*, $C_6H_3MeCl\cdot PCl_4$, crystal-
lises in pale yellow needles; when treated with sulphurous anhydride,
it yields the *oxychloride*, $C_6H_3MeCl\cdot POCl_2$, which melts at 36° and
boils at 290—291°. When this is warmed with water, it is converted
into 2-*chlorotolyl-4-phosphinic acid*, $C_6H_3MeCl\cdot PO(OH)_2$, which melts
at 190°; the normal *silver*, and the *silver*, *barium*, and *aniline
hydrogen* salts of this acid, all of them anhydrous, were analysed;
when the acid is heated with bromine and water, it is converted into
phosphoric acid and 2-chloro-4-bromotoluene (Willgerodt and
Salzmann, Abstr., 1889, 985); when it is dissolved in fuming nitric
acid, and the solution is diluted with water, the product is a
yellowish *mononitro*-derivative, melting at 200° and exploding at a
higher temperature, of which the yellow *barium hydrogen* and normal
lead and *silver* salts were analysed; when it is oxidised with alkaline
permanganate at 50—60°, it yields 2-*chlorobenzo-4-phosphinic acid*,
$COOH\cdot C_6H_3Cl\cdot PO(OH)_2$, melting at 254°, of which the *barium
hydrogen* salt was analysed.   C. F. B.

a- and β-**Trimethylphosphortolubetaines, and their Carb-
oxylic Acids.** By FR. CONEN (*Ber.*, 1898, **31**, 2919—2924).—
1 : 3-Xylylchlorophosphine, $C_6H_3Me_2\cdot PCl_2$ (Weller, Abstr., 1887, 824),
which consists of a mixture of two isomerides [$PCl_2 = 4$, (*a*); and pro-
bably 5, (*β*)], was converted by treatment with pure zinc methyl
into *dimethylxylylphosphine*, $C_6H_3Me_2\cdot PMe_2$, which boils at 233° (a
little *dimethylxylylphosphine oxide*, $C_6H_3Me_2\cdot PMe_2O$, was also obtained
as a syrup; the crystalline *mercurichloride* of this,

$$C_6H_3Me_2\cdot PMe_2(OH)_2 + HgCl_2,$$
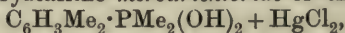
was analysed); from this phosphine, the phosphonium iodide,
$C_6H_3Me_2\cdot PMe_3I$, was prepared by treatment with methylic iodide in
ethereal solution. By fractional crystallisation, this iodide was
separated into two isomerides; the less soluble melts at 265°, and was
identified as 1 : 3-*xylyl-4-phosphonium iodide* (*a*) since it could also be
prepared from 1 : 3 : 4-mercurydixylyl. From it, a crystalline, hygro-
scopic, alkaline hydroxide was prepared by treatment with moist silver
oxide, and from this the hygroscopic *chloride*, $C_6H_3Me_2\cdot PMe_3Cl$,
melting at 110°. When oxidised with the theoretical quantity of
potassium permanganate at 55°, this chloride yields the deliquescent
betaine chloride, $COOH\cdot C_6H_3Me\cdot PMe_3Cl$, of which the orange-yellow
platinochloride was analysed; by treating the betaine chloride with
sodium carbonate, a-*trimethylphosphortolubetaine*, $C_6H_3Me\underset{PMe_3}{\overset{-CO-}{<}}>O$,
was obtained; this is very hygroscopic; the *nitrate* and golden-yellow
picrate melt at 226° and 220° respectively. When the phosphonium
chloride is oxidised at 60—70° with the amount of permanganate
necessary to convert both methyl groups into carboxyl, the crystal-
line *chloride*, $PMe_3Cl\cdot C_6H_3(COOH)_2$, is obtained (the *platinochloride*
melts at 258°); by treating this with the calculated quantity of
moist silver oxide, a-*trimethylphosphortolubetainecarboxylic acid*,

$COOH \cdot C_6H_3 \underset{PMe_3}{\overset{-CO->}{<}} O$, is formed ; this melts at $160°$; its blue *copper salt*, $OH \cdot PMe_3 \cdot C_6H_3 \cdot [COO]_2' Cu$, was analysed.

The more soluble of the two phosphonium iodides mentioned above melts at $205°$; it is the β- (probably $1:3:5$) compound. A series of analogous derivatives was prepared from it; of these, the *betaine-carboxylic* acid melts at $115°$.　　　　　　　　　　C. F. B.

Primary Chlorostibines of the Aromatic Series. By J. HASENBÄUMER (*Ber.*, 1898, **31**, 2910—2914. Compare Michaelis and Reese, Abstr., 1886, 885).—When mercury diphenyl and antimony trichloride are heated together at $130°$ in xylene solution, triphenyl-stibine chloride, $SbPh_3Cl_2$, and some diphenylstibine chloride, $SbPh_2Cl_3 + H_2O$, are formed. By heating triphenylstibine with antimony chloride and a little xylene at $240°$ for 48 hours continuously, *phenylchlorostibine*, $SbPhCl_2$, can be obtained, which melts at $58°$ and boils at $290°$, and emits a very unpleasant odour when heated ; aqueous sodium carbonate converts it into *phenyl-stibine oxide*, $SbPhO$, which melts at $150°$, whilst with alcoholic ammonium sulphide, it yields *phenylstibine sulphide*, $SbPhS$, which melts at $65°$. When it is saturated with gaseous hydrogen chloride in ethereal solution, crystalline, hygroscopic *phenyltetrachlorostibine* is obtained, and when this is dissolved in caustic soda, *phenylstibic acid*, $SbPhO(OH)_2$, is formed ; this is an amorphous powder which decomposes above $200°$, and dissolves in alkali carbonates and ammonia as well as in caustic alkalis; its anhydrous *barium hydrogen* salt, which forms a white precipitate, was analysed.

Paratolylchlorostibine, which was prepared in a similar manner, melts at $93·5°$, boils above $360°$, and yields a series of analogous deriva-tives ; of these, the *oxide* melts at $200°$.　　　　　　C. F. B.

Phenoxyacetic Acid. Phenylic Phenoxyacetate and its Bromo-derivatives. By ALB. J. J. VANDEVELDE (*Chem. Centr.*, 1898, i, 988—989 ; from *Bull. Acad. roy. Belg.*, [iii], **35**, 223—237).—*Phenoxyacetic chloride*, $OPh \cdot CH_2 \cdot COCl$, is prepared by warming a mixture of 100 grams of phenoxyacetic acid with 145 grams of phosphorus pentachloride, the fraction which boils at 160—$170°$ under 60 mm. pressure being rectified at the ordinary pressure. It is a colourless, fuming liquid, boils at 225—$226°$, and acts on water with violence. *Phenylic phenoxyacetate*, $OPh \cdot CH_2 \cdot COOPh$, is obtained by the action of phenoxyacetic chloride on phenol. The product after being washed with sodium hydroxide solution and water and distilled, yields a fraction which boils at $236°$ under 73 mm., or at 320—$325°$ under the ordinary pressure, and solidifies to a butyraceous mass ; it can be crystallised from chloroform, and is soluble in the ordinary organic solvents. It is not attacked by sodium carbonate in the cold, but is hydrolysed on heating. With phenylhydrazine in alcoholic solution, it forms crystals of *phenoxy-acetophenylhydrazide*, which melts at $180°$. By the action of bromine (1 mol.) dissolved in carbon bisulphide, carbon tetrachloride or chloro-form on phenylic phenoxyacetate (1 mol.), *phenylic parabromophenoxy-acetate*, $C_6H_4Br \cdot O \cdot CH_2 \cdot COOPh$, is formed ; it crystallises from ether, melts at $73°$, is insoluble in water, soluble in the ordinary organic

solvents, and is hydrolysed by boiling sodium carbonate solution. With an alcoholic solution of phenylhydrazine, it yields *parabromophenoxyacetylphenylhydrazide*, $C_6H_4Br\cdot O\cdot CH_2\cdot CO\cdot N_2H_3Ph$, which separates from boiling alcohol in white crystals and melts at 174°.

Parabromophenylic phenoxyacetate, $OPh\cdot CH_2\cdot COO\cdot C_6H_4Br$, obtained by the action of parabromophenol on phenoxyacetic chloride, separates from chloroform in colourless crystals, melts at 98°, and is soluble in the ordinary organic solvents, but insoluble in water. It is hydrolysed by hot sodium carbonate solution, and with phenylhydrazine yields the same compound as phenylic phenoxyacetate. *Parabromophenoxyacetic chloride*, $C_6H_4Br\cdot O\cdot CH_2\cdot COCl$, prepared by the action of phosphorus pentachloride on bromophenoxyacetic acid, boils at 259°, reacts violently with water, and when cooled forms a butyraceous mass which melts at 42°; with phenol, in presence of phosphorus oxychloride, which prevents the formation of resinous substances, it yields phenylic parabromophenoxyacetate.

E. W. W.

Derivatives of Orthotoluonitrile. By WILLY LANDSBERGER

(*Ber.*, 1898, **31**, 2880—2889).—*Paranitro-orthotoluonitrile*,

$$CN\cdot C_6H_3Me\cdot NO_2 \quad [Me : CN\cdot NO_2 = 1 : 2 : 4],$$
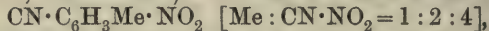
obtained when the orthonitrile (6 grams) is gradually added to well-cooled fuming nitric acid (30 c.c.), and the resulting yellow solution poured on to ice, crystallises from boiling alcohol in needles, melts at 105°, sublimes at 100° in long, slender needles, is readily soluble in acetone, chloroform, ethylic acetate, benzene, and hot alcohol, sparingly in ether, carbon bisulphide, acetic acid or hot water, and almost insoluble in light petroleum. When warmed for about $1\frac{1}{2}$ hours with 10 times its weight of concentrated sulphuric acid, it yields *nitrotoluamide*, which crystallises from boiling water in glistening needles, melts at 173°, and is only sparingly soluble in ether or light petroleum. When hydrolysed with fuming hydrochloric acid, it yields 4-nitro-orthotoluic acid. *4-Amido-orthotoluonitrile*, is obtained when an alcoholic solution of the nitro-derivative is reduced with tin and hydrochloric acid until a portion of the solution yields no oil on pouring into water. The base crystallises from boiling light petroleum in colourless, felted needles melting at 88°, and readily turning brown on exposure to the air. The *hydrochloride*, $C_8H_8N_2,HCl$, crystallises from absolute alcohol in yellowish, glistening needles melting at about 220°; the *picrate* crystallises in lemon-yellow needles and melts at 177—179°, and the *platinochloride* decomposes slowly above 240°.

Orthocyanobenzylaniline, $CN\cdot C_6H_4\cdot CH_2\cdot NHPh$, is obtained when orthocyanobenzylic chloride (6 grams) is added to aniline (14 c.c.) heated to 90°, and the mixture kept at that temperature for an hour; it is then rendered alkaline, the excess of aniline distilled in steam, and the product precipitated with potassium hydroxide and recrystallised from alcohol; it melts at 124—126°, and is insoluble in water, but readily dissolves in benzene, acetone, or alcohol. The *hydrochloride* turns grey at 120°, and completely decomposes at 238°. The *picrate* crystallises in yellow needles melting at 186°, and the *platinochloride* decomposes at about 223°.

Attempts have been made to prepare orthocyanobenzaldehyde by

Berg's method (Abstr., 1898, i, 553), but on warming a solution of orthocyanobenzylaniline hydrochloride with excess of sodium hypochlorite, crystals of orthocyanobenzylaniline chlorate,

$$CN \cdot C_6H_4 \cdot CH_2 \cdot NHPh, HClO_3,$$
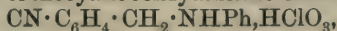
are obtained, they melt at 171°, again solidify, and on further heating decompose. When orthocyanobenzylaniline is oxidised with potassium permanganate at 15—20°, the chief product is phthalanil,

$$C_6H_4 \!\!<\!\!{}^{CO}_{CO}\!\!>\!\!NPh.$$
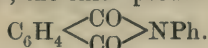
Ethylic β-orthocyanophenyl-α-methylpropionate,
$$CN \cdot C_6H_4 \cdot CH_2 \cdot CHMe \cdot COOEt,$$
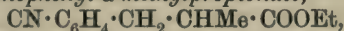
is obtained when ethylic methylacetoacetate (4·8 grams) is added to a 2N-alcoholic sodium solution (17 c.c.) and then, to this, a solution of orthocyanobenzylic chloride (5 grams) in absolute alcohol (20 c.c.); after 90 hours, only some 75 per cent. of the alkali is used up. The ethereal salt, which is isolated by distillation, passes over last of all; it boils at about 270°, and is practically insoluble in concentrated hydrochloric acid. It is hydrolysed when heated with concentrated hydrochloric acid for 2 hours at 100°, and the *β-orthocyanophenyl-α-methylpropionic acid* formed crystallises from boiling water in colourless needles melting at 99°; it is readily soluble in most solvents with the exception of carbon bisulphide. *β-Orthocarboxyphenyl-α-methylpropionic acid*, $COOH \cdot C_6H_4 \cdot CH_2 \cdot CHMe \cdot COOH$, formed when the ethylic salt is hydrolysed with concentrated hydrochloric acid at 160°, crystallises from hot water in colourless prisms melting at 142°. Its *silver* salt crystallises in minute needles. All attempts to obtain hydrindone derivatives from it have proved fruitless.

β-Orthocyanophenyl-α-ethylpropionic acid, crystallises from boiling water in glistening plates melting at 67—68°, and its *silver* salt melts at 180°. *β-Orthocarboxyphenyl-α-ethylpropionic acid* is readily soluble in most organic solvents, and crystallises from hot water in long, colourless, glistening needles melting at 140—141·5°.　　　　J. J. S.

Ethylic α-Phenylacetoacetate. By WALTER BECKH (*Ber.*, 1898, **31**, 3160—3164.)—Ethylic α-phenylacetoacetate cannot be obtained in any quantity by the action of ethylic acetate on ethylic phenylacetoacetate in presence of sodium ethoxide, the chief products of the reaction being ethylic acetoacetate and ethylic diphenylacetoacetate. It can, however, be obtained from *acetobenzylic cyanide*, $CH_3 \cdot CO \cdot CHPh \cdot CN$, which is formed by the action of ethylic acetate on benzylic cyanide in presence of sodium ethoxide, and is a dazzling white, crystalline mass melting at 90°. When this compound, in solution in absolute ethylic alcohol, is treated with hydrogen chloride, the free hydrogen chloride then removed by exposing the solution over solid potash, and the residue warmed with the calculated amount of water, *ethylic α-phenylacetoacetate*, $CH_3 \cdot CO \cdot CHPh \cdot COOEt$, is produced, a yield of about 55 per cent. of the theoretical being obtained. It is a colourless oil which boils at 145—147° under a pressure of 11 mm., and readily undergoes the characteristic hydrolysis of the ethereal salts of the ketonic acids,

yielding phenylacetic acid or benzyl methyl ketone, according to the hydrolytic agent employed.

Ethylic sodiophenylacetoacetate is an extremely hygroscopic powder; the *phenylhydrazone* crystallises in white needles melting at 104°, and is readily converted by boiling glacial acetic acid into 1 : 4-*diphenyl-3-methyl-5-pyrazolone*, $CMe\begin{smallmatrix}N-\!-\!-NPh\\ |\\ CHPh\cdot CO\end{smallmatrix}$, which crystallises in white needles melting at 196°. A. H.

Supposed Identity of Tannin and Digallic Acid. By PAUL WALDEN (*Ber.*, 1899, **31**, 3167—3174).—a-Digallic acid, prepared according to Schiff's directions, by the action of arsenic acid on gallic acid dissolved in alcohol, has no definite melting point, but sinters at 120° and begins to decompose at 150°; it dissolves readily in acetone, ethylic acetate, ethylic and amylic alcohols, and in acetic acid. Its molecular weight in boiling acetone is about 316, whilst the molecular weight of tannin, obtained from Schuchardt, was 1350—1560, that of another sample, obtained from Merck, being about 753—763, that is to say, 2 to 4 times as great as that of digallic acid (compare Paternò, Abstr., 1890, 105, and Sabanéeff, Abstr., 1891, 145).

The affinity coefficient of a-digallic acid is $K = 0.0012$; that of tannin varies greatly with the concentration, and is very much smaller than the above number.

When tannic acid, dissolved in dilute alcohol, is titrated with N/20 baryta water in presence of phenolphthalein, a cloudy, blood-red liquid is formed, whilst digallic acid, under similar circumstances, gives a clear, reddish liquid; in neither case is the end reaction definite.

Spectrometric examination of solutions of tannin and digallic acid shows that their absorptive powers for all regions of the spectrum are entirely different, the extinction coefficient of tannin being always considerably lower than that of digallic acid. When a 10 per cent. solution of tannin is mixed with a 5 per cent. alcoholic solution of arsenic acid, the whole liquid sets to a transparent, glass-like mass, which does not liquefy when warmed, but darkens when strongly heated, and, when dried, is insoluble in most of the usual media, but dissolves in soda and is reprecipitated on addition of mineral acids; the addition of arsenic acid also causes a speedy reduction of the rotatory power of the solution. If a solution of digallic acid be treated in a similar manner, it remains liquid for months.

The above facts, as well as those observed by other workers in this field, make it clear that there is no longer any reason whatever to suppose that tannin and digallic acid are identical. A. L.

Sacchareins. A New Class of Colouring Matters Derived from Orthobenzoic Sulphinide. By PAUL MONNET and J. KŒTSCHET (*Bull. Soc. Chim.*, 1897, **17**, [iii], 690—702).—Orthobenzoic sulphinide ("saccharin") condenses with phenols, forming products whose constitutions are of a type similar to that of the phthaleins. Thus, with phenol, the product has the constitution $C_6H_4\begin{smallmatrix}C(C_6H_4\cdot OH)_2\\ \diagdown\\ SO_2\end{smallmatrix}NH$,

and dissolves in alkali, giving a red solution which is decolorised on the addition of acids.

Resorcinol and orthobenzoic sulphinide interact at 200—220° in presence of aluminium chloride; the crude product, after treatment with dilute aqueous sodium carbonate, is a brownish-red mass whose solution in hot dilute alkalis has a marked orange-yellow colour, and, on dilution, exhibits a powerful green fluorescence. The colouring matter is precipitated by acids, and can be purified by dissolving it in alcohol and reprecipitating with water; it forms a brown resin which cannot be crystallised, has a metallic lustre, and is insoluble in water, but very readily soluble in alcohol. The *triacetyl* derivative, $C_{25}H_{19}SO_8N$, is a yellow, crystalline powder, and melts at 286°; its constitution is probably represented by the formula $SO_2{<}{}^{N\,Ac}_{C_6H_4}{>}C{<}{}^{C_6H_3(OAc)}_{C_6H_3(OAc)}{>}O$.

On saponification, the acetyl compound yields the pure "*saccharein*," $SO_2{<}{}^{NH\cdot}_{C_6H_4}{>}C{<}{}^{C_6H_3(OH)}_{C_6H_3(OH)}{>}O$, which crystallises in salmon-coloured scales, melts at 265—267°, dissolves in water and alcohol, and is soluble in alkalis, forming a pure yellow solution, having a green fluorescence; it is reprecipitated as a flocculent mass on the addition of acids. It yields halogen derivatives under the influence of bromine or iodine and sodium chlorate; the *bromo*-derivative is a crystalline powder, insoluble in water, but sparingly soluble in alcohol, which dissolves in alkalis, giving a beautiful red solution; the *iodo*-derivative is an orange-red powder which dissolves in alkalis, giving reddish-violet solutions. The product formed when "saccharin" is condensed with diethylmetamidophenol at 165°, is isolated by treating the resulting mass with sodium carbonate and then with soda, the insoluble residue being dissolved in hydrochloric acid. The *hydrochloride* separates in small, green crystals having a metallic lustre, dissolves readily in water, giving a solution which is violet-red and has a yellow fluorescence, but when this is heated to boiling it is decolorised, a flocculent, violet-tinted precipitate being formed.

The free *base*, $SO_2{<}{}^{NH\cdot}_{C_6H_4}{>}C{<}{}^{C_6H_3(NEt_2)}_{C_6H_3(NEt_2)}{>}O$, is colourless, crystallises from toluene or benzene, melts at 243°, is rather soluble in alcohol, benzene, toluene, and xylene, very readily in chloroform, and is insoluble in light petroleum. The *sulphate* closely resembles the hydrochloride.

The *saccharein* of *dimethylmetamidophenol* may be made by a method similar to that used in the foregoing case, and its properties resemble those of the corresponding substance; that of *monethylmetamidophenol* has similar properties, but it gives yellower solutions and imparts a colour to unmordanted cotton; it gives a colourless *acetyl* compound. The *saccharein* of *metahydroxydiphenylamine* gives salts which are insoluble in water but dissolve in alcohol, forming a violet-red solution.

Acetyltetrethylmetamidophenolsaccharein,

$$SO_2{<}{}^{N\,Ac}_{C_6H_4}{>}C{<}{}^{C_6H_3(NEt_2)}_{C_6H_3(NEt_2)}{>}O,$$
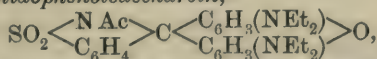
is a colourless, crystalline powder, and may be purified by crystal-

lisation from acetone; it melts at 230—232°, dissolves readily in hot, acidified water, is very soluble in benzene, fairly so in alcohol, chloroform, and ether, and is nearly insoluble in light petroleum; the solution in alcohol or chloroform is red, whilst that in light petroleum or ether is nearly colourless. It is easily saponified by alcoholic soda, the colour of the solution changing to an intense bluish-violet. *Ethyltetrethylmetamidophenolsaccharein,*

$$SO_2 {<}{NEt \atop C_6H_4}{>} C {<}{C_6H_3(NEt_2) \atop C_6H_3(NEt_2)}{>} O,$$
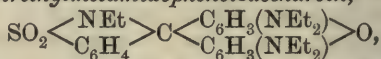
made by the action of ethylic iodide and sodium ethoxide on tetrethylmetamidophenolsaccharein, is colourless, dissolves readily in benzene, sparingly in ether and alcohol, and melts at 220—222°. The salts are more unstable than those of the parent substance, being somewhat readily decomposed by boiling water.   A. L.

1 : 5-Diketones. By EMIL KNOEVENAGEL (*Annalen,* 1898, **303,** 223—257. Compare Abstr., 1896, i, 210).—[With H. HOFFMANN.]— *Ethylic piperonylidenediacetoacetate,* $C_{20}H_{24}O_8$, obtained from piperonal and ethylic acetoacetate (2 mols.) in presence of diethylamine, crystallises from alcohol in small, white needles, and melts at 146—147°. Hydroxylamine converts it into the *oxime* $C_{20}H_{23}NO_7$, arising from the ethereal salt by elimination of $2H_2O$ and formation of a cyclohexenone ring; it melts and decomposes at 202°. *Ethylic 1-methyl-3-piperonyl-5-cyclohexenone-2 : 4-dicarboxylate,* $C_{20}H_{22}O_7$, produced on passing hydrogen chloride into ethylic piperonylidenediacetoacetate suspended in alcohol, crystallises from alcohol, and melts at 102°. 1-*Methyl-3-piperonyl-5-cyclohexenone,* $C_{14}H_{14}O_3$, is obtained by the action of boiling, 10 per cent. caustic potash on ethylic piperonylidenediacetoacetate, and crystallises from petroleum in white needles melting at 84—85°; the *oxime* melts and decomposes at 137°.

Ethylic orthonitrobenzylidenediacetoacetate, $C_{19}H_{23}NO_8$, from ethylic acetoacetate and orthonitrobenzaldehyde, crystallises from alcohol in white needles and melts at 163—164°.

[With ALFRED SCHÜRENBERG.]—*Ethylic metanitrobenzylidenediacetoacetate* melts at 146°; the *oxime* and *phenylhydrazone* melt at 201° and 161° respectively. 1-*Methyl-3-metanitrophenyl-5-cyclohexenone,* $C_{13}H_{13}NO_3$, is prepared by the action of boiling 40 per cent. sulphuric acid on ethylic metanitrobenzylidenediacetoacetate, which, along with the para-compound, differs from other 1 : 5-diketones in yielding cyclohexenones under the influence of acids rather than of alkalis; it melts at 98°, whilst the *oxime* and *phenylhydrazone* melt at 176° and 135—150° respectively. β-*Metanitrophenylglutaric acid,* $C_{11}H_{10}NO_6$, obtained by the action of moderately heated 5 per cent. caustic soda, melts at 205—206°; prolonged treatment with boiling alkali yields the same product associated with a small quantity of methylnitrophenylcyclohexenone.

[With H. HOFFMANN.]—*Ethylic paranitrobenzylidenediacetoacetate* melts at 170—171°; the *oxime* and *phenylhydrazone* melt at 208° and 214—215° respectively. *Ethylic 1-methyl-3-paranitrophenyl-5-cyclo-hexenonecarboxylate,* $C_{16}H_{17}NO_5$, obtained by treating the foregoing ethereal salt with boiling 20 per cent. sulphuric acid, melts at 119°,

whilst a 40 per cent. solution yields 1-*methyl*-3-*paranitrophenyl*-5-*cyclohexenone*, which crystallises from dilute alcohol in white needles, and melts at 134° ; the *oxime* and *phenylhydrazone* melt at 179—180° and 173° respectively. *β-Paranitrophenylglutaric acid* separates from alcohol in colourless crystals, and melts at 235°.

[With K. WEDEMEYER.] — *Ethylic cuminylidenediacetoacetate*, $C_{22}H_{30}O_6$, melts at 137°. Hydrogen chloride converts it, if suspended in alcohol, into *ethylic* 1-*methyl*-3-*isopropylphenyl*-5-*cyclohexenone*-2 : 4-*dicarboxylate*, $C_{22}H_{28}O_5$, which crystallises from alcohol and melts at 112° ; the *oxime*, which melts and decomposes at 188°, is also obtained by the action of hydroxylamine on ethylic cuminylidenediaceto-acetate. 1-*Methyl*-3-*isopropylphenyl*-5-*cyclohexenone* melts at 27°, and boils at 210·5 under a pressure of 17 mm.; the *oxime* melts at 124°.

Ethylic furfurylidenediacetoacetate, $C_{17}H_{22}O_7$, crystallises from petroleum, melts at 72°, and develops an intense violet-red coloration with ferric chloride; the *oxime* of the corresponding cyclohexenone compound obtained by the action of hydroxylamine melts and decomposes at 142°. *Ethylic* 1-*methyl*-3-*furfuryl*-5-*cyclohexenonecarb-oxylate*, $C_{14}H_{16}O_4$, melts at 72°, and boils at 194° under a pressure of 9 mm.; the *oxime* melts at 110—112°. 1-*Methyl*-3-*furfuryl*-5-*cyclo-hexenone* is a colourless liquid which boils at 153—154° under a pressure of 10 mm.; it has a sp. gr. = 1·1056 at 16°/4°, and the refractive index n_D = 1·5354. The *oxime* melts at 96—98°.

[With W. GOECKE.]—*Ethylic anisylidenediacetoacetate*, $C_{20}H_{26}O_7$, melts at 137° ; hydroxylamine converts it into the *oxime* of the corres-ponding cyclohexenone compound, which crystallises from alcohol and melts at 195°. *Ethylic* 1-*methyl*-3-*paramethoxyphenyl*-5-*cyclohexenone*-2 : 4-*dicarboxylate*, $C_{20}H_{24}O_6$, melts at 103°. 1-*Methyl*-3-*paramethoxy-phenyl*-5-*cyclohexenone*, $C_{14}H_{16}O_2$, melts at 65°; the *oxime* melts at 108°.

[With A. GROOS.] — *Ethylic methylsalicylidenediacetoacetate*, $C_{20}H_{26}O_7$, melts at 125° ; hydroxylamine converts it into the *oxime* of the corresponding cyclohexenone compound, which crystallises from xylene in stellate aggregates of white needles and melts at 145°. *Ethylic* 1-*methyl*-3-*orthomethoxyphenyl*-5-*cyclohexenone*-2 : 4-*dicarboxylate* $C_{20}H_{24}O_6$, crystallises from alcohol, and melts at 113°. 1-*Methyl*-3-*ortho-methoxyphenyl*-5-*cyclohexenone*, $C_{14}H_{16}O_2$, crystallises from petroleum in cubes, and melts at 51°; the *oxime* crystallises from dilute alcohol in white leaflets, and melts at 133°.

[With R. WEISS.]—*Ethylic parachlorobenzylidenediacetoacetate*, $C_{19}H_{23}ClO_6$, crystallises from alcohol in slender, white needles, and melts at 150—151° ; hydroxylamine converts it into the *oxime* of the corresponding cyclohexenone, which melts at 187—188°. *Ethylic* 1-*methyl*-3-*parachlorophenyl*-5-*cyclohexenone*-2 : 4-*dicarboxylate*, $C_{19}H_{21}ClO_5$, melts at 100—101°. 1-*Methyl*-3-*parachlorophenyl*-5-*cyclo-hexenone*, $C_{13}H_{13}ClO$, crystallises from petroleum in colourless needles, and melts at 59—60° to a viscous liquid which boils at 205—206° under a pressure of 12 mm. Hydroxylamine gives rise to two pro-ducts, the *oxime*, $C_{13}H_{14}NOCl$, and the abnormal *oxime*, $C_{13}H_{17}N_2O_2Cl$; these componnds melt at 154° and 197° respectively. M. O. F.

Hydroxydiphenylene Ketone. By GEORG HEYL (*Ber.*, 1898, 31, 3033—3035. Compare Staedel, Abstr., 1895, i, 233).—The author has prepared certain derivatives of symmetrical diorthodiamidobenzophenone. The *diacetyl* derivative melts at 154°. *Diorthiodobenzophenone*, $CO(C_6H_4I)_2$, crystallises in white, lustrous leaflets, and melts at 106—107°. The *diazo*-compound, $CO(C_6H_4 \cdot N_2 \cdot SO_4H)_2$, forms small, white needles and decomposes at 111—112°; it develops a carmine-red coloration with α-naphthol.

The following derivatives of hydroxydiphenylene ketone are also described. The *oxime* and *phenylhydrazone* melt at 169—170° and 173—174° respectively, whilst the *acetyl* and *benzoyl* derivatives melt at 130—131° and 128—129° respectively. The *benzylic, methylic,* and *ethylic* ethers melt at 93—94°, 141·5—142·5°, and 99—100° respectively; the *phenylcarbamate* melts at 148—149.

When fused with potash, hydroxydiphenylene ketone yields orthophenylsalicylic acid; the *methylic* salt is an oil, but the *ethylic* salt crystallises in white leaflets and melts at 46—47°.

Orthophenylmethylsalicylic acid [2-*methoxydiphenyl*-1-*carboxylic acid*], $OMe \cdot C_6H_3Ph \cdot COOH$, and *orthophenylethylsalicylic acid* [2-*ethoxydiphenyl*-1-*carboxylic acid*], $OEt \cdot C_6H_3Ph \cdot COOH$, are liquid. *Hydroxyfluorene alcohol*, $\overset{C_6H_4-}{\underset{CH(OH)}{\Big>}} C_6H_3 \cdot OH$, obtained by reducing hydroxydiphenylene ketone, crystallises in white needles melting at 201—201·5°.   M. O. F.

Benzilorthocarboxylic Acid. By CHARLES A. SOCH (*J. Physical Chem.*, 1898, 2, 364—370).—The author has studied the conditions of equilibrium for the two modifications of benzilorthocarboxylic acid. The yellow modification melts at 141·5°, whilst the white form melts at 125—130°, and changes over to the yellow form; the white modification is stable below 65°, and the yellow crystals are stable between 65° and 132°. The temperature of the unstable eutectic point is about 112°. Raising the initial temperature of heating first lowers and then raises the apparent freezing point. The percentage of the white modification in the melt increases with rising temperature; at some temperature between 65° and 132°, the heat of transformation is zero.   H. C.

Condensation Products of Phenylisocrotonic Acid: Isomeric Lactones of γ-Ketonic Acids. By JOHANNES THIELE (*Annalen*, 1898, 303, 217—222. Compare Erlenmeyer, jun., and Lux, Abstr., 1898, i, 668).—The paper is a preliminary communication. Phenylisocrotonic acid undergoes condensation with benzaldehyde, yielding *dibenzylidenepropionic acid*, $CHPh \colon CH \cdot C(\colon CHPh) \cdot COOH$; cinnamaldehyde gives rise to 1 : 6-*diphenylhexatriene*-3-*carboxylic acid*, $CHPh \colon CH \cdot C(COOH) \colon CH \cdot CH \colon CHPh$; pyrocinchonic anhydride forms the *lactone*, $CHPh \colon CH \cdot CH \colon C \!\!<^{CMe}_{O \cdot CO}\!\! > CMe$. Phthalic anhydride yields the *lactone* $CHPh \colon CH \cdot CH \colon C \!\!<^{C_6H_4}_{-O-}\!\! > CO$, along with two iso-

meric *phthalylphenylisocrotonic acids*,

$$\text{CHPh:CH·C(COOH):C}\diagdown^{\text{C}_6\text{H}_4}_{\text{O}}\diagup\text{CO}.$$
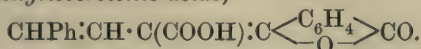
Bromine converts dibenzylidenepropionic acid into a *dibromide*, along with the unsaturated *lactone*, $\text{CHPh:C}\diagdown^{-\text{CH}}_{\text{COO}}\diagup\text{CPh}$, which, on hydrolysis, yields *phenacylcinnamic acid*, $\text{COPh·CH}_2\text{·C(:CHPh)·COOH}$, and this, on reduction, gives rise to *phenacylhydrocinnamic acid*, $\text{COPh·CH}_2\text{·CH(CH}_2\text{Ph)·COOH}$. When phenacylhydrocinnamic acid is treated with cold acetic anhydride containing a trace of sulphuric acid, the labile *lactone*, $\text{CH}_2\text{Ph·CH}\diagdown^{-\text{CH}}_{\text{COO}}\diagup\text{CPh}$, melting at $100\text{—}101°$ is produced; boiling acetic anhydride, however, converts phenacyl-hydrocinnamic acid into the stable *lactone*, $\text{CH}_2\text{Ph·C}\diagdown^{\text{CH}}_{\text{COO}}\diagup\text{CHPh}$, which melts at $67°$; both lactones are resolved by alkalis and by cold glacial acetic acid saturated with hydrogen bromide into phenacyl-hydrocinnamic acid. The formation of an α-unsaturated lactone from a γ-ketonic acid, and *vice versâ*, throws some doubt on the con-stitution of lactones hitherto regarded as unsaturated in the β-position.

Desylacetic acid is converted by cold acetic anhydride containing sulphuric acid into a labile *lactone*, $\diagup^{\text{CH}_2-\text{CO}}_{\text{CPh:CPh}}\diagdown\text{O}$, which melts at $100°$; hydrolysis with potash regenerates desylacetic acid, whilst boiling acetic anhydride converts it into diphenylcrotonolactone, which melts at $151·5°$, and probably has the constitution $\diagup^{\text{CH}-\!-\text{CO}}_{\text{CPh·CHPh}}\diagdown\text{O}$ (compare Klingemann, Abstr., 1892, 1002). It follows that the conversion of diphenylhydroxybutyrolactone into diphenylcrotonolactone proceeds on simpler lines than those indicated by Erlenmeyer, jun., and Lux (*loc. cit.*); the hydroxy-acid, $\text{C}_{16}\text{H}_{14}\text{O}_3$, probably has the constitution $\text{OH·CHPh·CPh:CH·COOH}$.　　　　M. O. F.

New Method for Transforming Paranitrodiaminotriphenyl-methanes into Rosanilines or their Leuco-bases. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1897, **17**, [iii], 654—659).—Paranitro-diamidotriphenylmethane or one of its derivatives is heated on the water-bath with a dilute solution of soda in weak alcohol for about an hour, the alcohol then distilled off, and the product isolated by the addi-tion of lime; it may be transformed into the corresponding rosaniline base by means of a suitable reducing agent.

When the above *product* is reduced with zinc-dust and a mineral acid, it gives a hydroxylamine compound; when dissolved in mineral acid or in acetic acid, it dyes cotton, mordanted with tannin or tartar emetic a bluish-violet; by the action of heat, the solution becomes greyish-blue, and wool or silk immersed in it becomes more or less violet-coloured; in the case of the tetralkyl derivatives, the cotton or silk is dyed a beautiful greenish-yellow. It behaves, therefore, like the basic colouring materials of the rosaniline group, that is to say the paranitro-compound is changed into the carbinol of the base by migra-

tion of an oxygen atom from the nitro-group; on the other hand, the formation of a hydroxylamine compound by its reduction shows that a $-NO$ or $=N \cdot OH$ group is still present. Its transformation into rosaniline by means of zinc and acetic acid also indicates the presence of a reducible azoxy-group and a carbinol group.

The constitution of the substance is either $NO \cdot C_6H_4 \cdot C(C_6H_4 \cdot NH_2)_2 \cdot OH$ or $C(C_6H_4 \cdot NH_2)_2 \underset{-O-}{\overset{-C_6H_4-}{<}} N \cdot OH$, the former representing it as a paranitrosocarbinol, and the latter as a derivative of quinoneoxime.

It is found that both substances exist in the product, and the leuco-bases may be separated by crystallisation. One gram of the leuco-base from the tetramethyl derivative is dissolved in water (80 grams) containing soda (10 grams) and alcohol (160 grams), and the whole heated on the water-bath for about half an hour; the liquid, when left to cool for 24 hours, deposits red crystals, whilst, later, yellow crystals separate, the amount being increased by the addition of brine.

The red substance turns brown at 85° and melts at 100—105°; the yellow substance melts at 142—143°. Both compounds afford tetra-methylrosaniline by reduction, and yield colouring matters on combination with phenols or alicyclic amines. The red substance dissolves in alcoholic acetic acid, giving a magnificent blue solution, and imparts a greenish-blue tint to cotton mordanted with tannin; the solution when heated gradually becomes a beautiful greenish-yellow. The yellow substance dissolves in acids, giving a nearly colourless solution, but on warming gives the same greenish-yellow solution as that obtained with the red substance. The red substance has the constitution represented by the first of the above formulæ, and the yellow that of the second.

The paper concludes with a brief discussion of the theoretical bearings of the above observations.   A. L.

Condensation of Benzylic Cyanide with Aromatic Alde-hydes: Symmetrical Triphenylglutaric Acid. By MARTIN HENZE (*Ber.*, 1898, **31**, 3059—3066).—Victor Meyer has shown (Abstr., 1889, 597) that benzylic cyanide and benzaldehyde interact in presence of sodium ethoxide, forming benzylidenebenzylic cyanide, $CHPh:CPh \cdot CN$; the latter condenses with more benzylic cyanide, affording the nitrile of triphenylglutaric acid, $CHPh(CHPh \cdot CN)_2$, which may be obtained from benzaldehyde in one step, by employing two molecular proportions of benzylic cyanide. Meta- and para-nitrobenzaldehyde and furfuraldehyde act in a similar way, but in the case of orthonitrobenzaldehyde and cinnamaldehydes, steric hindrance appears to come into play.

Triphenylglutaronitrile, $C_{23}H_{18}N_2$, which crystallises from a mixture of alcohol and ether in large, well formed crystals belonging to the cubic system, melts at 137—138°. When heated in a flask at 320°, it is slowly decomposed into benzylidenebenzylic cyanide and benzylic cyanide, a little hydrogen cyanide being also produced. When made in the above manner, it is accompanied by a very small quantity of a second substance, which melts at 153—155°.

Triphenylglutaric acid, $C_{23}H_{20}O_4$, is made by heating the nitrile

with fuming hydrochloric acid in closed tubes at 180—200°, when a small quantity of another substance, soluble in alkali, is also formed. It melts at 236—237°, crystallises from dilute alcohol in felted needles containing 1 molecule of alcohol of crystallisation, dissolves in alcohol, acetone, chloroform, and ethylic acetate, but is insoluble in water, benzene, ether, and light petroleum. The *silver* salt, $C_{23}H_{18}O_4Ag_2$, blackens slowly when exposed to light.

When attempts are made to hydrolyse triphenylglutaronitrile with alcoholic alkali, hydrolysis occurs, but further decomposition also takes place; in one instance, phenylacetic acid was detected, and an acid melting at 188—190°.

Triphenylglutaric anhydride, $C_{23}H_{18}O_3$, made by dissolving the acid in acetic chloride, exists in two forms; the first *modification*, obtained by the spontaneous evaporation of the acetic chloride solution crystallises in rectangular tablets and melts at 198—199°, whilst the second *modification*, produced when the first is boiled with acetone, crystallises in needles, and does not melt sharply, but sinters above 170° and is melted at 180°. The transformation of the latter into the former is effected by fusion or by dissolution in acetic chloride; both modifications afford the triphenylglutaric acid melting at 235—236°.

When hydrogen chloride is passed into a solution of triphenyl-glutaronitrile in dilute alcohol, one cyano-group appears to suffer partial hydrolysis. The *product* crystallises from alcohol, and on analysis gives numbers agreeing with the formula $CN \cdot CHPh \cdot CHPh \cdot CHPh \cdot CONH_2$. *Ethylic triphenylglutarate,* $C_{27}H_{28}O_4$, made by treating the free acid with alcohol and hydrogen chloride, is difficult to purify and melts at 95—110°.

When triphenylglutaronitrile is reduced with sodium and absolute alcohol, the products obtained are dibenzyl, phenylethylamine, and hydrogen cyanide; these probably result from an initial severance of the molecule, under the influence of alkali, into $CHPh{:}CPh \cdot CN$ and $CH_2Ph \cdot CN$, the former, by union with 4 atoms of hydrogen, affording $CH_2Ph \cdot CH_2Ph$ and HCN. A. L.

Anhydrobisdiketohydrindene (Bindone). By WILHELM WIS-LICENUS (*Ber.*, 1898, **31**, 2935—2938).—In reply to Ephraim (Abstr., 1898, i, 672), the author points out that the yellow compound described by himself and Reitzenstein (Abstr., 1894, i, 133) is only formed when anhydrobisdiketohydrindene is heated with acetic anhydride or alcoholic hydrogen chloride, and that it decomposes at 290—295°. It is not identical with the yellow compound formed when diketohydrindene ·is heated with the anhydro-derivative, and when the red condensation product of the latter is recrystallised from pyridine or boiled with alcohol. The author proposes to term the anhydro-compound *bindone*. A. H.

Colour Reactions of Indones and of Quinones with Malonic Acid Derivatives. By CARL LIEBERMANN (*Ber.*, 1898, **31**, 2903—2907. Compare Abstr., 1898, i, 682).—Dibromindone reacts with ethylic sodiomalonate, yielding ethylic bromindonemalonate,

$C_6H_4\underset{CBr}{\overset{CO}{<}}>C\cdot CH(COOEt)_2$, which in alkaline solution has a deep red colour. Dichloro- and dibromo-cinnamic acids do not yield similar products, but cyclic compounds, such as 2 : 3-dibrom-α-naphthaquinone, react yielding cornflower-blue products; but as these are unstable in alkaline solution, it is necessary to precipitate immediately with acetic acid. The product from 2 : 3-dibrom-α-naphthaquinone crystallises from alcohol in yellow needles which turn blue on the addition of a trace of alkali.

Dibromo-β-naphthaquinone yields a bluish-green solution with ethylic sodiomalonate, which, when acidified, yields a resinous compound crystallising from alcohol in orange-yellow needles; monobromo- and monochloro-β-naphthaquinone behave in a similar manner. The colours are, as a rule, extremely evanescent in alkaline solution, and rapidly become destroyed. Chlorinated quinones also react with malonic acid derivatives in a similar manner (compare Stieglitz, Abstr., 1891, 455; Jackson and Grindley, Abstr., 1893, i, 563), as also do the simple quinones themselves. Benzoquinone, with a solution of ethylic sodiomalonate, yields evanescent colours; α-naphthaquinone gives a greenish-blue, and β-naphthaquinone a red colour. J. J. S.

2-Bromoflavone. By STANISLAUS VON KOSTANECKI and A. LUDWIG (*Ber.*, 1898, **31**, 2951—2953).— 5-*Bromo*-2-*acetoxybenzylideneacetophenone*, $OAc\cdot C_6H_3Br\cdot CO\cdot CH:CHPh$, obtained when the corresponding hydroxy-compound (Abstr., 1898, i, 371) is heated with acetic anhydride and anhydrous sodium acetate, crystallises from alcohol in colourless needles melting at 115—116°, and yields a *dibromide*, $C_{17}H_{13}Br_3O_3$, which crystallises from alcohol in glistening plates melting at 121—122°. The dibromide, when treated with the requisite quantity of potassium hydroxide solution and then poured into water, yields a flocculent precipitate of 2-*bromoflavone*, $C_6H_3Br\underset{CO\cdot CH}{\overset{O---CPh}{<}}$, which crystallises from alcohol in colourless needles melting at 189—190°, and dissolves in concentrated sulphuric acid, yielding a colourless, non-fluorescent solution. Flavone itself, when quite pure, also gives a colourless solution with sulphuric acid, but this exhibits a marked violet-blue fluorescence, the former statement (Abstr., 1898, i, 584) being incorrect. Bromoflavone, when hydrolysed with a concentrated solution of sodium ethoxide, yields benzoic acid and 5-bromo-2-hydroxyacetophenone. J. J. S.

Benzoin Yellow. By CARL GRAEBE (*Ber.*, 1898, **31**, 2975—2979). —The author has investigated the yellow dye obtained by the condensation of benzoin with gallic acid (D.R.P. 95739, *Chem. Centr.*, 1898, i, 870). To prepare it, benzoin is added to a solution of gallic acid in sulphuric acid (66° B) kept at 0—5° and after being stirred during 24 hours, the mixture is poured into water, when the dye is precipitated; it crystallises from a mixture of alcohol and acetic acid in yellow needles, decomposes at about 250°, is readily soluble in sodium hydroxide, and dissolves slowly in sodium carbonate solution. The *acetyl* derivative, $C_{21}H_{10}O_4Ac_2$, crystallises in pale yellow needles melting at 237°. The *lead* salt, when dried at 150°, has the composi-

tion $C_{21}H_{10}O_4Pb$. Benzoin-yellow, when distilled with zinc dust, yields anthracene, and, when oxidised with nitric acid (sp. gr. $= 1\cdot3$), yields benzoic and phthalic acids in nearly equal quantities. When fused with sodium hydroxide, it yields benzoic acid, and when suspended in chloroform and treated with bromine gives a *dibromide* which crystallises from acetic acid and decomposes at 221—$222°$. The constitution given to benzoin yellow is

$$\begin{matrix} C_6H_4\cdot C === CPh \\ | \\ CO—C_6H(OH_2) \end{matrix} \!\!>\!\!O \ [O:(OH)_2:CO = 1:2:3:4].$$
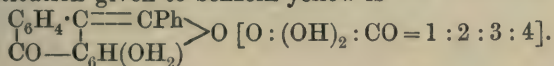
<div align="right">J. J. S.</div>

Action of Hydrazine Hydrate on Phenols. By L. Hoffmann (*Ber.*, 1898, 31, 2909—2910).—When α- or β-naphthol is heated with excess of hydrazine hydrate for 6 hours at $160°$, α- or β-naphthyl-hydrazine is formed. With phenol, the condensation takes place less easily; at $160°$, only phenoldiammonium, $C_6H_5\cdot OH, N_2H_4$ (Curtius and Thun, *J. pr. Chem.*, 1876, [ii], 14, 190) is formed, but at $220°$ a small quantity of phenylhydrazine is obtained.　　　C. F. B.

Syntheses by means of Orthophthalyl Tetrachloride (m. p. 88°). I. Preparation of Diphenylanthrone. By Albin Haller and Alfred Guyot (*Bull. Soc. Chim.*, 1897, [iii], 17, 873—879).—*Di-phenylanthrone*, $CO\!<\!\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!\!>\!CPh_2$, is prepared by the action of alumi-nium chloride on a solution in benzene of phthalyl tetrachloride (m. p. 88°); the chlorides of anthraquinone and of phenyloxanthranol are intermediate products, and can be used for preparing the substance. The authors ascribe to the phthalyl tetrachloride the formula $CCl_3\cdot C_6H_4\cdot COCl$, and as small quantities of diphenylanthrone are produced in the condensation of commercial phthalyl dichloride with benzene, it is probable that the dichloride contains a certain amount of this tetrachloride. Diphenylanthrone melts at $192°$, crystallises from glacial acetic acid in colourless needles and from benzene in large, transparent prisms, is insoluble in water, and dissolves only slightly in boiling alcohol, ether, and light petroleum. The molecular weight, as determined by the cryoscopic method, was 320 to 325 (calc. 346). The substance does not react with phenylhydrazine or with hydroxyl-amine; on crystallising from nitrobenzene, large, transparent tablets of a pale yellow colour are obtained, which have the composition $2C_{26}H_{18}O + C_6H_5\cdot NO_2$. The *chloride of phenyloxanthranol*,

$$CO\!<\!\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!\!>\!CPhCl,$$
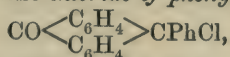
prepared by warming diphenylphthalide with phosphorus pentachloride, crystallises from benzene in large, colourless, transparent prisms, and melts at $164°$. When heated with water in sealed tubes, it is converted quantitatively into phenyloxanthranol, whilst with alcohols it yields the corresponding ethers.　　　T. M. L.

The Rendering Active ("Activirung") of Oxygen. II. The Active Oxygen of Oil of Turpentine. By Carl Engler and J. Weissberg (*Ber.*, 1898, 31, 3046—3055).—Pure pinene is oxidised

by air or oxygen in exactly the same way as is crude turpentine. The chemical activity of turpentine exposed to oxygen does not depend on the formation of ozone or of atomic oxygen, as the substance retains its properties for years if kept in the dark, which would not be the case if such powerful oxidising substances were present. Berthelot has shown that only the dissolved oxygen is driven out when inert gases are led through the active liquid (*Ann. Chim. Phys.*, 1860, [iii], 58, 426), and it is found that the residue left after distilling the greater part of the pinene in a vacuum still has strong oxidising powers. The substance gives a yellow coloration with a solution of titanic acid in sulphuric acid, and a brown coloration with vanadic acid, reactions which are exhibited by most peroxides, but not with ozone. If, moreover, oxidising substances of this kind owed their activity to active oxygen, their oxidising powers should be similar, which is by no means the case.

The activity cannot, on the other hand, be due to the presence of hydrogen peroxide, for Kingzett (this Journ., 1874, 511 ; 1875, 210) has shown that the active substance cannot be extracted by water, and Löw has observed (*Zeit. f. Chem.*, [ii], 6, 609) that iodine is liberated when oxidised turpentine is shaken with a solution of potassium iodide, a reaction not shown by hydrogen peroxide. It is now found that it does not afford the characteristic blue solution when shaken with chromic acid solution and ether, whilst an equivalent amount of hydrogen peroxide, added to turpentine and treated in the same manner, gives a decided indication of its presence. The presence of hydrogen peroxide, observed by most experimenters, is doubtless due to the presence of water in the original oil. It is not necessary, however, that water should be present, as turpentine which has been dried by means of sodium and phosphorus pentoxide rapidly absorbed dry oxygen.

The activity of the oil is not proportional to the amount of oxygen absorbed, hence a certain quantity of the latter is used up in a more profound oxidation of the turpentine. Experiments made on the action of oxygen on turpentine at various temperatures have shown that, at about 100°, the oil is rendered active most rapidly, and that, at 140—160°, the active oxygen disappears, being, doubtless, used up in the further oxidation of the substance, an action which also goes on slowly at 80—100°.

The authors express their views of the actions which go on in the following manner, representing the turpentine by A.

$$A + O_2 = A{<}{^O_O} = A{\ll}{^O_O}.$$
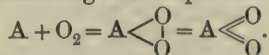
If the second of these changes is not intramolecular, but intermolecular, unaltered turpentine being attacked, the equation then becomes $AO_2 + A = 2AO$.

The action of the peroxide, $A{<}{^O_O}$, on easily oxidisable substances is represented as $AO_2 + B = AO + BO$.

The action of water on peroxides is briefly discussed, and the

production of hydrogen peroxide is attributed to formation of an intermediate hydrate which affords hydrogen peroxide by intra-molecular change.   A. L.

Citral (Geranial) and Lemon-grass Oil. By FRIEDRICH W. SEMMLER (*Ber.*, 1898, **31**, 3001—3003).—The author says " Stiehl's citriodoraldehyde, as well as his geranial and allolemonal (this vol., i, 66) yielded in my hands, when sufficiently purified, one and the same geranial, with absolutely identical physical properties, and with identical derivatives. . . . I must still maintain the identity of citral with the geranial obtained by me by oxidising geraniol."

     C. F. B.

Citral. By OSCAR DOEBNER (*Ber.*, 1899, **31**, 3195—3197).—The author has shown that lemon-grass oil contains 80—82 per cent. of citral (Abstr., 1898, i, 676); according to Stiehl, however (this vol., i, 66), the oil contains three isomeric aldehydes, namely, citral (10 per cent.), citriodoraldehyde (40—50 per cent.) and allolemonal (25—30 per cent.). In view of this discrepancy, the author has examined the portions of the oil to which the last two names are given by Stiehl. "Citriodoraldehyde" is nearly pure citral, as when treated with pyruvic acid and β-naphthylamine it gives a large quantity of citryl-β-naphthacinchonic acid, together with a small quantity of a second acid which melts, while still impure, at 230°. Allolemonal consists of a mixture of about equal parts of aldehydic and non-aldehydic constituents, and the former, after separation by the bisulphite method and treatment with pyruvic acid and β-naphthylamine, gives only citryl-β-cinchonic acid. Crude allolemonal gives also methyl-cinchonic acid and another acid which is sparingly soluble in alcohol, and melts indefinitely at 210—235° (Stiehl gives the melting point of allolemonyl-β-naphthacinchonic acid as 235°); this impure acid resolves itself on recrystallisation into the citrylic acid, methyl-β-naphthacinchonic acid, and, probably, also, a neutral condensation product of pyruvic acid and β-naphthylamine, melting at 232°, which is easily obtained by warming them together in alcoholic solution for a short time. The author's former results are therefore completely confirmed.   A. L.

Orientation in the Terpene Series. XXIII. Hydroxy-carone and Ketoterpin. By ADOLF VON BAEYER and CONRAD BAUMGÄRTEL (*Ber.*, 1898, **31**, 3208—3217).—Optically active 1 : 8-*hydroxybromotetrahydrocarvone* is obtained as its sodium deriva-tive when Wallach's brominated dihydrocarvone hydrobromide (1 : 8-dibromotetrahydrocarvone, Abstr., 1894, i, 536) is diluted with ether and shaken with sodium hydroxide (sp. gr. = 1·23) for about an hour. The sodium salt is decomposed with dilute sulphuric acid, and the hydroxybromotetrahydrocarvone rapidly filtered, as it is converted both by water and dilute acid into ketoterpin. When recrystallised from dry ether or a mixture of amylene and light petroleum, it is obtained in large prisms, melts at 69—72°, is readily soluble in most solvents, and is somewhat unstable, being decomposed both by acids

and alkalis. When recrystallised from methylic alcohol, a small quantity of a substance melting at 136—138° is obtained, and this contains the same amount of bromine as the hydroxybromo-compound. An active *hydroxycarone*, $C_{10}H_{16}O_2$, formed when hydroxy-bromotetrahydrocarvone (1 mol.) is treated with a solution of potassium hydroxide (1·5 mols.) in methylic alcohol, is a viscous oil distilling at 134−135° under 19 mm. pressure, and dissolves somewhat readily in water, the solution having a feebly acid reaction ; with concentrated caustic soda, it gives crystals of the sodium derivative. Its *oxime* forms large, glistening prisms melting at 138° ; its *semicarbazone,* glistening needles melting at 197°, and its *phenylurethane* crystallises from alcohol in four-sided prisms melting and decomposing at 190°. The carone ring in hydroxycarone is readily ruptured, even in the cold, by dilute acids ; hydrobromic acid gives Wallach's *d*-dibromo-tetrahydrocarvone, whilst hydrochloric acid gives the corresponding dichloro-derivative melting at 41—42°.

Optically active ketoterpin is readily obtained when hydroxycarone is gradually treated with ice cold dilute sulphuric acid, the solution neutralised with sodium carbonate, and extracted with ether and alcohol ; it crystallises from ether in prisms, melts at 78—80°, distils at 163—165° under a pressure of 16 mm., and dissolves readily in water, alcohol, or chloroform, but when pure is only sparingly soluble in ether ; a 37 per cent. alcoholic solution has a rotatory power = −32·5°. The same compound can also be obtained directly from hydroxybromotetrahydrocarvone. When boiled with dilute sulphuric acid, it is completely converted into carvacrol. Its *sodium* derivative, $C_{10}H_{17}O_3Na$, crystallises in small needles, and is reconverted into the ketoterpin by water or alcohol ; its *oxime,* $C_{10}H_{19}NO_3$, melts at 163° ; its *semicarbazone* at 184—185°, and its *phenylhydrazone* melts and decomposes at 150—160°.

When reduced with sodium and alcohol, ketoterpin yields 1 : 2 : 8-*trihydroxyterpan*, which, when distilled under diminished pressure and recrystallised from ether or chloroform, forms six-sided plates melting at 97—98°, and readily soluble in water, alcohol, &c. A 20 per cent. alcoholic solution has a rotatory power of −55°. When oxidised with chromic anhydride and sulphuric acid, the trihydroxy-compound yields an active methyl ketone of homoterpenylic acid melting at 48—49°.

<div align="right">J. J. S.</div>

Carvenone. By FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1898, 31, 2889—2899).—When carvenone, which, according to the authors, is most readily obtained by Baeyer's method (Abstr., 1894, i, 535), is oxidised with a 2 per cent. alkaline solution of potassium permanganate (3 atoms of oxygen to 1 molecule of carvenone), the chief products are, α-methylglutaric acid, 2 : 6-dimethyl-heptan-5-onoic acid, $CHMe_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot COOH$, and α-hy-droxy-α′-methyl-α-isopropyladipic acid,

$$CHMe_2 \cdot C(OH)(COOH) \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot COOH.$$
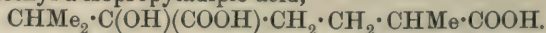
From 40 grams of carvenone, about 36 grams of the mixed acids are obtained, lower fatty acids are removed by distillation with steam,

and the residue dissolved in ether and extracted several times with an amount of sodium carbonate solution insufficient to neutralise all the acid present. The first extracts contain the stronger acids, the neutral solution of these is boiled with excess of copper acetate when the sparingly soluble copper salt of α-methylglutaric acid is precipitated. The filtrate, when acidified, yields α-hydroxy-α′-methyl-α-isopropyl-adipic acid, which is the chief oxidation product, and when freed from acetic acid gradually solidifies; after repeated crystallisation from water, it melts at 136—137°. It yields a sparingly soluble *silver* salt, and when heated just above its melting point loses water and yields a *lactonic acid*, $C_{10}H_{16}O_4$, melting at about 100°. When gently oxidised, the acid, $C_{10}H_{18}O_5$, is converted into 2 : 6-dimethylheptan-4-onoic acid. The latter acid is also obtained from the last sodium carbonate extracts, as it is a very feeble acid; it is an oil, and does not solidify at −20°, but distils at 166—168° under 14 mm. pressure. It yields an *oximido*-derivative, $C_9H_{16}O_2$:N·OH, melting at 67—68°, and sparingly soluble in water. When further oxidised, it yields acetone and α-methylglutaric acid.

The constitution of carvenone which is most in harmony with the formation of these oxidation products is

$$CHMe_2 \cdot C {<}^{CH—CO}_{CH_2 \cdot CH_2} {>} CHMe.$$
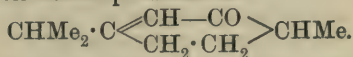
Wallach's hydroxylamine derivative melting at 162—163° would then have the constitution $^{CHMe_2}_{HO \cdot NH} {>} C {<}^{CH_2 \cdot C(NOH)}_{CH_2—-CH_2} {>} CHMe,$ and when oxidised yields the nitroso-derivative,
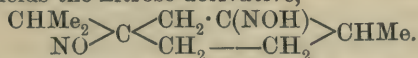
$$^{CHMe_2}_{NO} {>} C {<}^{CH_2 \cdot C(NOH)}_{CH_2——CH_2} {>} CHMe. \qquad \text{J. J. S.}$$

Solubility of Camphor. By CONSTANTIN I. ISTRATI and AL. J. ZAHARIA (*Compt. rend.*, 1898, 127, 557—559).—Camphor, contrary to the usual statements, is slightly soluble in water; a saturated solution has a sp. gr. = 1·00071 at 15°, and, in a tube 22 cm. long is dextrorotatory $[\alpha]_D = +0·4°$. In concentrated hydrochloric acid, camphor dissolves much more readily at 0° than at higher temperatures; 100 c.c. of a saturated solution contains, at 0°, 40·276 grams of camphor. On warming the solution by the heat of the hand, camphor is deposited, but, on again cooling, this redissolves; on diluting the solution, camphor separates. It is suggested that camphor probably dissolves in concentrated hydrochloric acid owing to the formation of the *compound* $C_8H_{14} {<}^{CCl \cdot OH}_{CH_2}$, and that this is decomposed either by heat or by the addition of water. $\qquad$ W. A. D.

Oxidising Action of α-Chlorocamphor. By H. VITTENET (*Bull. Soc. Chim.*, 1897, [iii], 17, 705).—When α-chlorocamphor is heated at 200° with aromatic amines, it undergoes decomposition, the bases being oxidised, with formation of small quantities of the usual characteristic colouring matters. Thus a mixture of toluidine and xylidine gives a magenta, diphenylamine gives diphenylamine-blue, α-naphthylamine affording α-naphthamein. $\qquad$ A. L.

Picrotoxin. By RICHARD JOS. MEYER and P. BRUGER (*Ber.*, 1898, **31**, 2958—2974. Compare Paternò and Oglialoro, this Journal, 1877, i, 719; ii, 790; Abstr., 1879, 729; 1881, 440; Barth and Kretschy, Abstr., 1881, 286; 1882, 412; 1884, 846; Schmidt, Abstr., 1881, 740; 1884, 845).—Pikrotoxin is an astringent principle of the fruit of *Menisperum cocculus.* The commercial product usually melts between 192° and 200°, but after recrystallisation from water invariably yields a product melting at 199—200°; it is extremely bitter and very poisonous, producing similar effects to those obtained with strychnine. Paternò and Oglialoro, Schmidt, and others regard it as a definite compound which is readily decomposed into pikrotoxinin and pikrotin, but, according to the authors, it is merely a mixture of these two in definite, but not molecular, proportions, namely, 54—55 per cent. of pikrotoxinin and 45—46 of pikrotin. It may be partially separated into the two constituents by boiling with benzene or chloroform, or by treatment with barium hydroxide; the only method which gives anything like quantitative results is that with bromine water.

Pikrotoxinin, $C_{15}H_{16}O_6$, is best obtained from pikrotoxin by brominating the latter, when in hot aqueous solution, with a slight excess of bromine water, and then, by means of zinc dust and acetic acid, removing the bromine from the monobromopikrotoxinin, which crystallises out; it crystallises from hot water in colourless, anhydrous needles, but from cold aqueous solutions in rhombic plates containing $1H_2O$, melts at 200—201°, is readily soluble in all the usual solvents on warming, and also in cold alcohol or chloroform; it is also soluble in alkalis, but is not reprecipitated on the addition of acids. Sulphuric acid develops an intense orange-red coloration, and when hydrogen chloride is led into an ethereal solution of the compound, polymerisation occurs, and *pikrotoxide*, melting at 308—310°, is formed. Aqueous solutions reduce ammoniacal silver nitrate in the cold, but it contains neither an aldehydic nor a ketonic group. It has an extremely bitter taste, and is the active principle of pikrotoxin; its specific rotatory power $[\alpha]_D = -5.85°$.

Bromopikrotoxinin, $C_{15}H_{15}BrO_6$, which is most readily obtained by adding bromine water to a hot, nearly saturated aqueous solution of pikrotoxinin until the solution remains permanently yellow, may be purified by recrystallisation from absolute alcohol; it separates in glistening needles, melts at 259—260° (Schmidt gives 250—255°; Paternò and Oglialoro give 240—250°), and has $[\alpha]_D^{17} = -132.5°$.

Chloropikrotoxinin crystallises from alcohol in a mixture of needles and plates melting at 272°.

Iodopikrotoxinin, obtained by the action of iodic acid and a solution of iodine in potassium iodide on a hot aqueous solution of pikrotoxinin, crystallises from alcohol in colourless needles and melts at 198—199°.

Bromopikrotoxic acid, $C_{14}H_{16}BrO_5 \cdot COOH + H_2O$, is obtained when 10 per cent. potassium hydroxide solution is slowly added to finely divided bromopikrotoxinin suspended in 10 times its weight of boiling water until all has dissolved; on the addition of hydrochloric acid, the acid crystallises out in colourless needles melting at

245—246°; it has no bitter taste and is optically active $[a]_D = -62.6°$. The *calcium* salt, $(C_{15}H_{16}BrO_7)_2Ca + 5H_2O$, *potassium* salt, with $2H_2O$, *ammonium* salt, and *mercurous* salt have been prepared. *Pikrotoxic acid*, $C_{15}H_{18}O_7$, obtained in small amount by the removal of bromine from the bromo-acid by the aid of sodium amalgam in alkaline solution, crystallises from water in needles melting at 229—230°, and has no bitter taste; its aqueous solution has strong reducing properties, and it readily undergoes decomposition in both aqueous and ethereal solution.

The substance obtained by Paternò and Oglialoro by the action of sodium acetate and acetic anhydride on pikrotoxin and described as an unsaturated acid, is shown to be *diacetylpikrotoxinin*, $C_{15}H_{14}O_6Ac_2$, as it can readily be obtained by the action of acetic chloride on pikrotoxinin; it sublimes in slender needles melting at 254—255°, and forms an unstable compound with bromine.

Pikrotin, $C_{15}H_{18}O_7$, is best obtained from the filtrate from bromopikrotoxinin, part separating out on cooling, whilst the remainder may be obtained by evaporation; it can be purified by several extractions with small quantities of hot chloroform, followed by recrystallisation from water; it forms small, felted needles, or thick, rhombic prisms melting at 248—250°, is readily soluble in absolute alcohol or acetic acid, but only sparingly in ether, chloroform, or benzene. Its specific rotatory power $[a]_D = -64.7°$, and it reduces Fehling's solution, &c., but only on warming. Its molecular formula has been established by molecular weight determinations and by the analyses of its benzoyl and acetyl derivatives.

Benzoylpikrotin, $C_{15}H_{17}O_7Bz$, crystallises from absolute alcohol in colourless needles, melts at 236°, and is readily soluble in chloroform, sparingly in ether or alcohol.

Dibenzoylpikrotin, obtained when pikrotin (1 mol.) is heated with benzoic chloride (3 mols.) at 190°, crystallises from alcohol in needles melting at 247—248°. When a large excess of benzoic chloride is employed, no definite product is obtained.

Acetylpikrotin, $C_{15}H_{17}O_7Ac$, crystallises from benzene, alcohol, or acetic acid in glistening plates melting at 244—245°, and is probably identical with the compound described by Paternò and Oglialoro as diacetylpikrotoxinin and melting at 227°. When pikrotin is allowed to remain in contact with acetic chloride for 24 hours at the ordinary temperature, and then heated until complete solution ensues, two compounds are obtained. *Anhydrodiacetylpikrotin*, $C_{15}H_{14}O_6Ac_2$, which is precipitated, on the addition of alcohol, in crystalline masses melting above 300°, and *diacetylpikrotin*, $C_{15}H_{16}O_7Ac_2$, which is obtained as an oil from the alcoholic mother liquor; when its hot, aqueous solution is allowed to cool, drops of oil separate, which solidify to crystalline needles melting at 207—210°; these contain $2H_2O$.

Attempts to convert pikrotin into pikrotoxinin by removal of the elements of water have not proved successful.

When warmed with fuming nitric acid, pikrotin yields a nitro-derivative, $C_{15}H_{15}O_6 \cdot NO_2$, *anhydronitropikrotin*, melting at 260°.

J. J. S.

Chlorophyll and its Derivatives. By Friedrich G. Kohl (*Chem. Centr.*, 1898, i, 992; from *Bot. Centr.*, 19, 417—426).— The author prepares Schunk's phyllotaonin by treating the green solution obtained by allowing blades of grass to remain immersed in alcoholic potassium hydroxide solution for a long time, with barium nitrate, filtering and washing the precipitate with boiling water, and then with boiling alcohol. The precipitate, unlike Schunk's phyllotaonin, is insoluble in alcohol, and the solution of pure chlorophyll-hydrochloric acid obtained from it by suspending it in water, treating with excess of hydrochloric acid, and precipitating the barium with sulphuric acid, does not yield the alkylic ether of phyllotaonin prepared by Schunk and Marchlewski. According to the author, phyllotaonin is a sodium compound of chlorophyll, and phylloxanthin is not a derivative of chlorophyll. E. W. W.

Condensation of Cyclic Acetone Bases with Mercaptans; Exceptions to the Rule of Mercaptole Formation. By Hermann Pauly (*Ber.*, 1898, 31, 3145—3151).—Vinyldiacetonamine reacts in the normal manner with ethylic and phenylic mercaptans. *Trimethylpiperidinediethylmercaptole hydrochloride,*

$$C(SEt)_2 \begin{matrix} CH_2 \cdot CHMe \\ CH_2 - CMe_2 \end{matrix} NH,HCl,$$
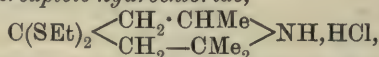
formed by the action of vinyldiacetonamine on ethylic mercaptan, crystallises, with $1H_2O$, in rectangular plates, whilst the anhydrous salt melts at 161—163°, and the free *base* is an oil. The mercaptole is readily converted by oxidation into *trimethylpiperidinediethylsulphonal,*
$C(SO_2Et)_2 \begin{matrix} CH_2 \cdot CHMe \\ CH_2 - CMe_2 \end{matrix} NH$, which forms small, feathery crystals melting at 135°; the *hydrochloride* and *platinochloride* are both crystalline. *Trimethylpiperidinediphenylmercaptole hydrochloride* crystallises in plates melting at 227°, whilst the free base melts at about 78° and forms sparingly soluble salts.
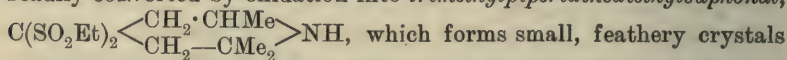
Triacetonamine, on the other hand, only reacts with 1 mol. of ethylic mercaptan, forming *triacetoninethylsulphide hydrochloride,*
$SEt \cdot C \begin{matrix} CH - CMe_2 \\ CH_2 \cdot CMe_2 \end{matrix} NH,HCl$, which forms small, rhombic crystals melting at 186°; the free *base* is a colourless oil, and the *platinochloride* crystallises in slender, yellowish needles. *Triacetoninephenylsulphide hydrochloride* crystallises in slender prisms melting at 187—188°; the free *base* is a colourless oil, but it unites with $1H_2O$ to form a hydrate which crystallises in prisms often a centimetre in length. It appears probable that this remarkable difference between the closely allied compounds, vinyldiacetonamine and triacetonamine, depends in some way on the difference in configuration of the groups immediately adjacent to the imido-group. A. H.
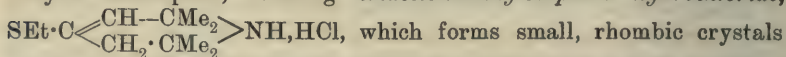
Pyridylacetonylchloride and Acetonylpiperidine. By Ernst Schmidt and Daniel Knuttel (*Arch. Pharm.*, 1898, 236, 580—601. Compare this vol., i, 4).—Pyridylacetonylchloride was prepared according to Dreser's directions (Abstr., 1894, i, 549) from pyridine and monochloracetone. Its *platinochloride* crystallises in dark orange

prisms melting at 206—207°, and its *aurichloride* in yellow needles melting at 141—143°. The *mercurichloride* crystallises in needles melting at 120°, but the double salts with copper and calcium chlorides are not well characterised substances.

When distilled with a solution of sodium carbonate, pyridylacetonyl chloride is converted into its components; with moist silver oxide or when heated alone, it undergoes a complicated decomposition with production of pyridine, and when acted on with sodium amalgam no piperidine derivative has so far been obtained.

Pyridylacetonyl chloride phenylhydrazone, prepared by heating together phenylhydrazine, and the chloride, separates from light petroleum in bunches of crystals melting at 133—134°. The *oxime* forms long, white, prismatic crystals melting at 182—184°; it does not reduce Fehling's solution, and gives a *platinochloride* melting at 204—205° with partial decomposition, and an *aurichloride* melting at 144—145°. The oxime is more stable towards silver oxide than pyridylacetonyl chloride, and attempts to bring about a rearrangement led to the following results. Concentrated hydrochloric and sulphuric acids decompose the oxime into its components; acetic chloride does not act on the oxime when heated under pressure, but when heated on a water-bath, it gives rise to a liquid *monacetyl* derivative, yielding an *aurichloride* melting at 140—141°, and a *platinochloride* melting at 195—197°; acetic anhydride converts the oxime into hydroxylamine and pyridineacetone chloride, and benzoic chloride or benzoic anhydride decompose it into its components.

When the oxime is reduced with sodium amalgam, pyridylacetonyl chloride is reformed, and when heated with ammonium formate, an amine is not produced, but a complicated reaction takes place with production of pyridine.

When piperidine and chloracetone are heated together in benzene solution, piperidine hydrochloride and a small amount of *acetonyl-piperidine*, $C_8H_{15}NO$, are produced; the latter yields an *aurichloride* in clear, yellow crystals melting at 106—107°, and a *platinochloride* in small, prismatic crystals melting at 179—180°.

Methylpiperidineacetonyl chloride, $C_5NH_{10}MeCl \cdot CH_2 \cdot COMe$, is obtained by the interaction of chloracetone and methylpiperidine. Its *aurichloride* melts at 86°, and the *platinochloride* crystallises in beautiful orange needles melting at 197—198°. A. W. C.

Formation of Chains. XXIX. Piperidine. By CARL A. BISCHOFF (*Ber.*, 1898, 31, 2839—2847).

[With STEFANOWSKI.]—*Ethylic piperidyloacetate*, $C_5NH_{10} \cdot CH_2 \cdot COOEt$, obtained when ethylic chloracetate is added to piperidine, or when benzene solutions of the two are mixed, is separated from the piperidine hydrochloride by the aid of ether, and forms an oil distilling at 209° under 732 mm. pressure. It is hydrolysed when heated with twice its weight of dry barium hydroxide in a salt bath for 10 hours. The acid, when recrystallised from chloroform and alcohol, forms well-developed, colourless prisms, part of which melts at 123—125°, and the residue remains solid even at 211°, this is due to the loss of water, as when dried at 125° the compound has the composition $C_7H_{13}NO'$

and then melts at 215—217°. Piperidyloacetic acid is soluble in water, alcohol, chloroform, and also in alkalis and acids.

[With MAISEL.]—Piperidine hydrobromide crystallises in oblong, rhombic plates melting at 235°.

Ethylic piperidylo-α-propionate, $C_5NH_{10}\cdot CHMe\cdot COOEt$, is a colourless oil distilling at 217°; when hydrolysed with barium hydroxide, it yields α-piperidylopropionic acid, which crystallises from absolute alcohol, with $3H_2O$. After drying at 100°, it melts at 205—206·5°, and is identical with Brühl's piperidyl-α-alanine (this Journ., 1876, i, 699). When heated at 222—240°, the acid evolves carbonic anhydride, and an oil, probably ethylpiperidine, is obtained; at temperatures above 240°, carbonic oxide is evolved, and an alkaline product melting at about 80° left.

[With KUSZELL.]—*Ethylic piperidylo-α-butyrate*,
$$C_5NH_{10}\cdot CHEt\cdot COOEt,$$
best obtained by treating ethylic α-bromobutyrate (1 mol.) with an excess of piperidine (3 mols.), is a colourless oil boiling at 222—223° under 753 mm. pressure. The free *acid*, after purification by dissolving it in alcohol and precipitating with ether, crystallises from water, with $\frac{1}{2}H_2O$, and melts at 106—107°; when dehydrated at 100°, it melts at 153—154·5°.

[With PAKIS.]—*Ethylic piperidylo-α-isobutyrate*, $C_5NH_{10}\cdot CMe_2\cdot COOEt$, boils at 217° under 750 mm. pressure; the *acid*, $C_5NH_{10}\cdot CMe_2\cdot COOH$, which does not solidify very readily, crystallises from hot chloroform, and melts at 160—161°.

Ethylic piperidylo-α-isovalerate, $C_5NH_{10}\cdot CHPr^\beta\cdot COOEt$, which is a thick, yellowish oil boiling at 228° under 752 mm. pressure, can only be hydrolysed by heating with barium hydroxide for $5\frac{1}{2}$ hours at 170—180° under 11—13 atmospheres pressure. The *acid*, after purification with benzene and chloroform, melts at 152—155°; dissolves readily in alkalis, acids, water, alcohol, or hot chloroform, but is only sparingly soluble in cold benzene, acetone, or carbon bisulphide, and insoluble in ether or light petroleum. The following list gives the percentage of reaction taking place between piperidine and the ethylic salts when 4·25 grams of the base is heated for 1 hour at 100° with equivalent quantities of the different ethylic salts. The extent to which the reaction had taken place was estimated by isolating the piperidine hydrobromide and weighing it. Ethylic bromopropionate, 91·1; ethylic bromobutyrate, 88·4; ethylic bromisobutyrate, 56·1; ethylic bromisovalerate, 49·4; ethylic phenylbromacetate, 50·6 per cent.

[With HOLM.]—The reaction between piperidine and the bromides of α-bromo-substituted fatty acids takes place with the greatest readiness. In this way, the following compounds have been prepared. *α-Bromopropiopiperidide*, $C_5NH_{10}\cdot CO\cdot CHMeBr$, boils at 150—152° under 10 mm. pressure, and when kept for some time at a low temperature solidifies to hygroscopic, rhombic plates melting at 30°; *α-bromobutyropiperidide* distils at 144—146° under 25 mm. pressure, and melts at 125—130°; *α-bromisobutyropiperidide* boils at 147—150° under 35 mm. pressure, and melts at 121·5—122·5°; *α-bromisovaleropiperidide* melts at 65°. In all four cases, the yields were practically theoretical.   J. J. S.

Formation of Chains. XXX. Carbazole, Amidoazobenzene, and Acetanilide. By CARL A. BISCHOFF (*Ber.*, 1898, **31**, 2847—2854).—As an ethereal solution of carbazole, when saturated with hydrogen bromide, yields no insoluble salt, the method adopted in the case of other bases (see preceding abstract), namely, heating two molecular proportions of the base with one of an ethylic salt of a bromo-fatty acid, and determining the extent to which the reaction had taken place, by weighing the amount of hydrobromide of the base formed, could not be employed. Instead, molecular quantities of carbazole and of the ethylic salts were heated together, but no very definite results were obtained. Better results were obtained when equivalent quantities of carbazole and of bromides of different bromo-fatty acids were heated in benzene solution. 6·7 grams of carbazole was heated to boiling with 160 c.c. of benzene, and then an equivalent quantity of the acid bromide, dissolved in 40 c.c. of benzene, added during the course of an hour, the mixture being finally heated for 5 hours in a reflux apparatus. The following percentage results were obtained : α-bromopropionic bromide, 87·94 ; α-bromobutyric bromide, 84·05 ; α-bromisobutyric bromide, 0 ; and α-bromisovaleric bromide, 72·88. The author attempts to explain these results by his dynamical hypothesis.

[With WALDMANN.]—α-*Bromopropionylcarbazole*,

$$C_{12}H_8N \cdot CO \cdot CHMeBr,$$

purified by crystallisation from hot light petroleum and ether, melts at 125° and is readily soluble in most organic solvents with the exception of cold alcohol, ether, or light petroleum. All attempts to condense ethylic α-bromobutyrate or phthalic anhydride with carbazole were fruitless.

[With KARUKOWSKI.]—α-*Bromobutyrylcarbazole* melts at 110° ; α-*bromisovalerylcarbazole* crystallises from alcohol in glistening needles melting at 130°.

[With HUREWITSCH.]—The reaction between paramidoazobenzene and the bromides of different bromo-fatty acids has been studied in the usual manner, using two molecules of the base to one of the bromide. *Paramidoazobenzene hydrobromide* crystallises from boiling water in violet-black, glistening crystals, melts at 206—207°, and is very sparingly soluble in ether, alcohol, or benzene. α-*Bromopropion-amidoazobenzene*, $NPh \vdots N \cdot C_6H_4 \cdot NH \cdot CO \cdot CHMeBr$, forms reddish-yellow, hair-like crystals, melts at 185°, and when heated with alcoholic potash yields a small amount of a compound melting at 227—228°, probably a *lactyl* derivative,
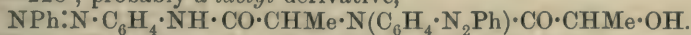
$$NPh \vdots N \cdot C_6H_4 \cdot NH \cdot CO \cdot CHMe \cdot N(C_6H_4 \cdot N_2Ph) \cdot CO \cdot CHMe \cdot OH.$$

[With KAISERSTEIN.]—α-*Bromobutyramidoazobenzene* crystallises from benzene in yellowish-red needles melting at 158° ; when heated on platinum foil, it gives violet fumes, and with alcoholic potash gives a pale-yellow, crystalline compound melting at 280°, and probably having a constitution analogous to that of the lactyl derivative mentioned above.

[With SOBOLEWSKI.]—The yield of α-*bromisobutyramidoazobenzene* is about 54 per cent. ; it crystallises from hot benzene in orange-red needles, melts at 167—168°, and, when treated with alcoholic potash,

yields *a-hydroxyisobutyramidoazobenzene* melting at 193°.   *a-Bromiso-valeramidoazobenzene* crystallises from dilute alcohol in orange-coloured needles melting at 190°.

Acetanilide (9 grams), benzene (150 c.c.), and a-bromopropionic bromide yield a small quantity of acetanilide hydrobromide melting at 152·5—153·5° and a-bromopropionanilide (compare Abstr., 1893, i, 51), the latter being probably formed by the hydrolysis of the primary condensation product.   The other bromides react with acetanilide in a similar manner.   J. J. S.

Formation of Indigo by Industrial Processes : Diastasic Functions of Indigo-yielding Plants.   By L. BRÉAUDAT (*Compt. rend.*, 1898, **127**, 769—771).—The author's experiments indicate that micro-organisms play no part in the indigotic fermentation of the leaves of *Isatis alpina*.   This plant, like *Indigofera anil* and other indigo-yielding species, contains a hydrolytic diastase and an oxydase ; in the presence of water, the former hydrolyses indican into indigo-white and indiglucin, whilst the latter, especially in alkaline solutions, oxidises the former compound into indigotin.   *Indigofera dosna*, which yields no indigo, contains neither indican nor oxydase.   G. T. M.

Action of Chloracetone on Quinoline and Allied Bases. By ERNST SCHMIDT and WILHELM GOEHLICH (*Arch. Pharm.*, 1898, **236**, 635—640).—*Quinolylacetonyl chloride*, $C_9H_7NCl\cdot CH_2\cdot COMe$, was obtained by heating a mixture of quinoline and monochloracetone in molecular proportion ; it yields a *platinochloride*, as a light brown, amorphous precipitate melting with decomposition at 224—226° ; and an *aurichloride* crystallising from water containing hydrogen chloride, in golden yellow needles melting at 164—165°.

Only tetrahydroquinoline hydrochloride results from the interaction of monochloracetone and tetrahydroquinoline ; with methylquinoline, a similar action takes place, but a small amount of *methylquinolylace-tonyl chloride* is also produced ; its platinochloride crystallises in plates melting at 230°.

Isoquinoline reacts readily with monochloracetone, giving rise to *isoquinolylacetonyl chloride*, which crystallises from alcohol, and yields a *platinochloride* crystallising in yellowish-red needles melting at 221—223°, and an *aurichloride* as yellow, glistening needles, melting at 141°.

Codeine does not react with monochloracetone in a similar manner.
                                                                  A. W. C.

Pyrazole from Acetylene and Diazomethane.   By HANS VON PECHMANN (*Ber.*, 1898, **31**, 2950—2951).—Acetylene, purified by washing with lead acetate solution and dried with sulphuric acid and calcium chloride, is passed into a stoppered flask containing an ethereal solution of diazomethane and surrounded by ice ; the flask is occasionally shaken, and at the end of two days, although the yellow colour of the diazomethane has not entirely disappeared, a yield of 50 per cent. of pyrazole, $\begin{smallmatrix} CH\cdot NH \\ CH\cdot CH \end{smallmatrix}\!\!>\!N$, is obtained when the ethereal solution is evaporated.   J. J. S.

Isomeric Chlorophenyldimethyl Pyrazoles. By AUGUST MICHAELIS and HANS RÖHMER (*Ber.*, 1899, **31**, 3193—3195).—When 1-phenyl-3 : 4-dimethyl-5-pyrazole is heated at 150—160° with $1\frac{1}{2}$ molecular proportions of phosphorus oxychloride in a closed tube, and the product purified by treatment with water, extraction with ether, and distillation under diminished pressure, 5-*chloro*-1-*phenyl*-3 : 4-*dimethyl-pyrazole*, $\begin{array}{c} CMe=N \\ | \quad\quad >NPh \\ CMe:CCl \end{array}$, is obtained; it is a feeble base, boils at 147° under a pressure of 12 mm., and dissolves in strong hydrochloric acid, but is reprecipitated on the addition of water; when reduced with sodium and alcohol, it yields a pyrazoline, which gives a very stable red coloration with sulphuric acid and potassium dichromate.

When antipyrine is heated with phosphorus oxychloride at 160° for 12 hours, it yields a compound isomeric with the above substance, which the authors term *antipyrinechloropyrazole*, $C_{11}H_{11}N_2Cl$; it behaves towards hydrochloric acid in the same way, but when reduced and treated with potassium dichromate and sulphuric acid, it gives a red coloration which quickly disappears. It appears to combine with 4 atoms of bromine, yielding a *compound* which melts at 130°; the latter is decomposed by warm soda, giving a crystalline *substance* which contains 1 bromine and 1 chlorine atom, and separates from dilute alcohol in very long needles melting at 52—53°.

A second product of the action of phosphorus oxychloride on antipyrine is a *substance* which is not extracted when the aqueous liquid is shaken with ether, but can be isolated by adding soda, evaporating to dryness, and extracting the residue with absolute alcohol, when the latter, on evaporation, deposits a considerable quantity of the substance, in the form of colourless, shining crystals, which do not give the reactions of antipyrine. A. L.

A Simple Conversion of Pyrazolones into Pyrazoles. By AUGUST MICHAELIS and HANS RÖHMER (*Ber.*, 1898, **31**, 2907—2908. Compare Abstr., 1891, 1068).—When 1-phenyl-3-methyl-5-pyrazolone (1 mol.) is heated with phosphorus oxychloride ($1\frac{1}{2}$ mols.) for 10 hours at 150°, 5-*chloro*-1-*phenyl*-3-*methylpyrazole* is formed, the yield being almost quantitative.

$$NPh\begin{array}{c} N=CMe \\ | \\ CO\cdot CH_2 \end{array} \longrightarrow NPh\begin{array}{c} N=CMe \\ | \\ CCl:CH \end{array}$$

This substance boils at 142° under 9 mm. pressure. C. F. B.

3-Hydroxy-1-phenyl-5-pyrazolone. By AUGUST MICHAELIS and HANS RÖHMER (*Ber.*, 1898, **31**, 3003—3014).—The substance described as 1-phenyl-3 : 5-pyrazolidone (Abstr., 1892, 1004) appears to be, in reality, 3-hydroxy-1-phenyl-5-pyrazolone, $\begin{array}{c} NPh\cdot CO \\ | \quad\quad\quad >CH_2 \\ N:C(OH) \end{array}$, for this constitution is most in harmony with the reactions described in the present paper. It is best obtained by allowing ethylic chloromalonate (30 grams, = 1 mol.) to remain with phenylhydrazine (3 mols.) for 3 days in a flask fitted with a Bunsen valve, dissolving the product in caustic

soda solution, extracting the solution carefully with ether several times, and then treating it with excess of hydrochloric acid, keeping it cool meanwhile. When (1 mol.) heated with phosphorus oxychloride (1 mol.) at 100° for 12 hours, it is converted into *3-chloro-1-phenyl-5-pyrazolone*, $\begin{array}{c} \text{NPh·CO} \\ | \quad\quad \\ \text{N} = \text{CCl} \end{array}\!\!>\!\text{CH}_2$, which melts at 143—144°; with benzaldehyde and with nitrous acid, it yields a *4-benzylidine* and a *4-isonitroso*-derivative respectively; these are both red, and melt at 108—109° and 146—147°; the latter crystallises with $2\,\mathrm{H_2O}$. When it is heated with 2 mols. of phosphorus oxychloride at 150° for 6 hours, the product is *3 : 5-dichloro-1-phenylpyrazole*, $\begin{array}{c} \text{NPh·CCl} \\ | \quad\quad \\ \text{N} = \text{CCl} \end{array}\!\!>\!\text{CH}$; this melts at 25—26° and boils at 170—172° under a pressure of 16 mm.

When 3-hydroxy-1-phenyl-5-pyrazolone is dissolved in caustic potash solution and treated gradually with methylic iodide, the solution being cooled meanwhile, *3-methoxy-1-phenyl-4-dimethyl-5-pyrazolone*, $\begin{array}{c} \text{NPh} - \text{CO} \\ | \quad\quad\quad \\ \text{N:C(OMe)} \end{array}\!\!>\!\text{CMe}_2$, is formed; this melts at 70° and boils at about 310°; when it is dissolved in caustic soda solution and hydrochloric acid added, a product $\left[\begin{array}{c} \text{NPh·C(OH)}_2 \\ | \quad\quad\quad\quad \\ \text{N} = \text{C(OMe)} \end{array}\!\!>\!\text{CMe}_2 ?\right]$ is precipitated which melts at 178° and contains $1\,\mathrm{H_2O}$ more than the original compound. When the methoxydimethyl compound (1 mol.) is heated with phosphoric chloride ($1\frac{1}{2}$ mols.) at 120—125°, methylic chloride is evolved and a *chlorophenyldimethylpyrazolone*, $\begin{array}{c} \text{NPh} - \text{CCl} \\ | \quad\quad\quad\quad \\ \text{N:C(OMe)} \end{array}\!\!>\!\text{CMe}$, is formed; this melts at 108—109° and boils at 150—160° under a pressure of 22 mm.; when crystallised from water, it unites with $1\,\mathrm{H_2O}$, forming a compound which melts at 173—174°. When the methoxydimethyl compound (1 mol.) is heated with phosphorus oxychloride ($1\frac{1}{2}$ mols.) at 150° for 10 hours, it yields an isomeric *chlorophenyl-dimethylpyrazolone*, $\begin{array}{c} \text{NPh·CO} \\ | \quad\quad \\ \text{N} = \text{CCl} \end{array}\!\!>\!\text{CMe}_2$, boiling at 170—172° under 22 mm. pressure, and less soluble in water than its isomeride; phosphorus oxychloride has no further action on this compound, but phosphoric chloride at 150° converts it into *3 : 5-dichloro-1-phenyl-4-methylpyrazole*, $\begin{array}{c} \text{NPh·CCl} \\ | \quad\quad \\ \text{N} = \text{CCl} \end{array}\!\!>\!\text{CMe}$, which boils at about 155° under a pressure of 16 mm.   C. F. B.
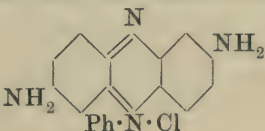
Action of Formaldehyde on Amarine. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1897, [iii], **17**, 864—865).—On adding formaldehyde to an alcoholic solution of amarine, the additive compound, $C_{21}H_{18}N_2,CH_2O$, is obtained in white needles which melt at 145°; like amarine itself, the compound is monobasic. The whole of the formaldehyde is removed on heating at 180°, and by treatment with aqueous ammonia at 100°, it is converted quantitatively into hexamethylenetetramine.

                                        T. M. L.

Nitro- and Amido-rosindulines. By FRIEDRICH KEHRMANN, FERD. RADEMACHER, and OTTO FEDER (*Ber.*, 1898, **31**, 3076—3087).— The influence of the introduction of amido-groups into different positions in the rosinduline molecule
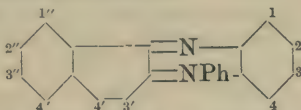
on the tinctorial properties of the dyes thus formed has been studied. The introduction of an amido-group into the para-position (2) with respect to azonium nitrogen gives a bluish-violet dye which does not fluoresce. The introduction of amido-groups into the phenyl group directly attached to azonium nitrogen alters the colour of the dyes very little, and the introduction of an amido-group in the para-position (4′) with respect to azine nitrogen, for example, as in the previously described naphthaphenosafranine, changes the colour slightly from red towards violet, it further increases the intensity of the colour and also the fluorescence. A similar difference is observed between naphthaphenosafranine and Nietzki-Otto's isorosinduline. Analogous differences may be observed in the safranines of the benzene series, so that it is safe to predict that the hitherto unknown isomeride of phenosafranine, namely,

is a violet to blue dye.

2-Nitrorosinduline chloride (compare Abstr., 1898, i, 155), when treated with sodium carbonate, yields the free base in the form of the *anhydride*, $NH <^{C_{10}H_5 \cdot N}_{NPh---} > C_6H_3 \cdot NO_2$; this is a dark, brownish-red precipitate decomposing at about 242°. The *platinochloride*,

$$C_{22}H_{15}N_4O_2PtCl_6,$$
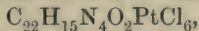
forms ruby-red plates with a golden lustre, and is practically insoluble in water. The *acetyl* derivative, $C_{24}H_{16}N_4O_3$, crystallises from a mixture of alcohol and benzene in reddish-brown needles, insoluble in water; its salts with mineral acids are somewhat yellower than those of the nitrorosindulines. The *dichromate, nitrate, iodide,* and *mercurichloride* derivatives are red, crystalline compounds almost insoluble in water.

2-*Amidorosinduline chloride* or 2 : 4′-*diamidophenylnaphthaphenazonium chloride*, obtained when the nitro-chloride is suspended in warm alcohol and reduced with tin and hydrochloric acid, crystallises in dark violet needles with a coppery lustre; to obtain it quite pure, it is dissolved in a little boiling water and a few drops of hydrochloric acid are added to the solution. It dissolves readily in water with a blue-violet, and in alcohol with a pure blue coloration. With acids, it forms three series of salts. Dissolved in concentrated sulphuric acid, it gives a *tri-acid* salt in the form of a green solution; when this is diluted with water, the colour changes to reddish-yellow, owing to the

formation of a *di-acid* salt, and when poured into much water or when the excess of acid is neutralised, a violet *mon-acid* salt is formed. The *platinochloride*, $(C_{22}H_{17}N_4Cl)_2PtCl_4$, is a dark blue, crystalline powder.

2-*Acetamido-4'-amidophenylnaphthaphenazonium chloride*, obtained by the action of acetic anhydride on the diamido-compound at ordinary temperatures, crystallises in small, brown needles and shows the same colour reactions as rosinduline, thus indicating that it is the amido-group in position 2, and not in position 4', which has been acetylated.

2 : 4'-*Diacetamidophenylnaphthaphenazonium chloride*, obtained by heating the diamido-compound or its monacetyl derivative with acetic anhydride and sodium acetate, crystallises in minute plates, with a yellow, metallic lustre. Its hot aqueous or alcoholic solution has a bright red colour and brick-red fluorescence. The *base* itself, $C_{26}H_{20}N_4O_2$, is obtained in the form of violet needles when the chloride is treated with sodium carbonate.

Paranitro-4'-amidophenylnaphthaphenazonium chloride is obtained when 3 grams of Nietzki and Baum's nitramidodiphenylamine (Abstr., 1896, i, 164) is suspended together with 2·2 grams of oxynaphthaquinonimide in 50 c.c. of alcohol containing 0·8 gram of hydrochloric acid (20 per cent.), and the mixture kept at the ordinary temperature during 3 months; the corresponding rosindone is formed at the same time, and may be removed by repeated extraction with hot benzene. The chloride resembles rosinduline chloride, but is somewhat yellower, and more sparingly soluble in water. The *base* itself crystallises in reddish-yellow needles decomposing at 260°.

4'-*Paradiamidophenylnaphthaphenazonium chloride*, $C_{22}H_{17}N_4Cl + 2H_2O$, crystallises in metallic-green prisms and is readily soluble in water; its aqueous and alcoholic solutions have a blood-red colour and a slight red fluorescence. The free *base* is readily transformed into the carbonate when left exposed to the air.

Paracetamidodinitrodiphenylamine, when reduced with ammonium sulphide, yields *acetamidonitro-orthamidodiphenylamine*,

$$NHAc\cdot\overset{4}{C_6H_4}\cdot NH\cdot\overset{4}{C_6H_3}(NO_2)\cdot\overset{2}{N}H_2,$$
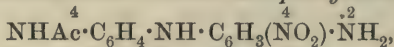
which crystallises from alcohol in golden, glistening scales, melting at 254—255°; this, when condensed with oxynaphthaquinonimide by the aid of hydrochloric acid, yields 2-*nitro-4'-paradiamidophenylnaphthaphenazonium chloride*, $C_{22}H_{16}N_5O_2Cl + 3H_2O$, which crystallises from alcohol in brick-red plates with a golden lustre; it is fairly readily soluble in water and alcohol, and yields a *monacetyl* derivative crystallising in dark red needles. The free *base* from this acetyl derivative sinters at 250°. The *diacetyl* derivative, $C_{26}H_{20}N_5O_4Cl$, forms light red crystals, and yields a violet-red base which sinters at 260—261°.

2 : 4'-*Paratriamidophenylnaphthaphenazonium chloride* crystallises in long, glistening, black-violet needles soluble in alcohol or water. The *base* forms violet-blue needles and appears to yield four series of salts.   J. J. S.

Nitro- and Amido-derivatives of Phenylisonaphthaphenazonium and of Methylnaphthaphenazonium. By FRIEDRICH KEHRMANN and HENRI JACOB (*Ber.*, 1898, **31**, 3087—3097).— Hydroxynaphthaquinonimide reacts with nitrophenylorthophenylene-

diamine, yielding rosinduline derivatives (see preceding abstract). 4-Acetamido-1 : 2-naphthaquinone reacts with an alcoholic solution of the sulphate of the same base, yielding two isomeric sulphates corresponding with the two chlorides,

$$\text{I. NHAc} \cdot \overset{4'}{\text{C}_{10}}\text{H}_5 \!\!\ll^{\text{N}\underline{\quad}}_{\text{NPhCl}}\!\!> \text{C}_6\text{H}_4 \cdot \overset{2}{\text{N}}\text{O}_2, \text{ and}$$

$$\text{II. NHAc} \cdot \overset{4'}{\text{C}_{10}}\text{H}_5 \!\!\ll^{\text{NPhCl}}_{\text{N}\underline{\quad}}\!\!> \text{C}_6\text{H}_4 \cdot \overset{3}{\text{N}}\text{O}_2.$$
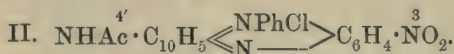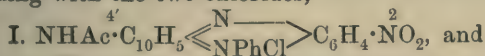
The former is identical with the sulphate obtained from oxynaphthaquinonimide and nitrophenylorthophenylenediamine sulphate. The two sulphates, which are accompanied by a bye-product insoluble in water, are precipitated as the chlorides, then hydrolysed with 50 per cent. sulphuric acid, and, when cold, the sulphate corresponding to I. crystallises out. The second sulphate is converted into the chloride, and is thus obtained in the form of blackish-green crystals; it may be recrystallised from 20 per cent. hydrochloric acid, but a small quantity is always converted into an insoluble brown isomeric chloride, probably having the constitution,

$$\text{N}\overset{\cdot\cdot}{\text{H}}:\overset{4'}{\text{C}_{10}}\text{H}_5\!\!\ll^{\text{NPhCl}}_{\text{-NH}\underline{\cdot}}\!\!>\text{C}_6\text{H}_4\cdot\overset{2}{\text{N}}\text{O}_2.$$
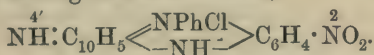
This compound is more readily obtained when a more dilute acid (5—10 per cent.) is employed. The brown isomeride is practically insoluble in alcohol or water, but dissolves in hot methylic alcohol, and when hydrogen chloride is passed into this solution, the brown salt becomes reconverted into the green. The free base corresponding with this chloride has not been isolated in a pure form. 4-Acetamido-1 : 2-naphthaquinone also reacts with nitromethylorthophenylenediamine hydrochloride, yielding two isomeric rosinduline derivatives; they are somewhat difficult to separate, but the one is rather more readily hydrolysed than the other. When boiled with alcohol, they yield *nitracetamidonaphthaphenazine*, decomposing between 295° and 300°. Hydroxynaphthaquinonimide reacts with nitromethylorthophenylenediamine hydrochloride, yielding 2-*nitro*-4'-*amidomethylnaphthaphenazonium chloride*, $\text{C}_{17}\text{H}_{13}\text{N}_4\text{O}_2\text{Cl}$, which crystallises from alcohol in metallic green needles, and is soluble in water or alcohol; its *platinochloride* and *aurichloride* form red, crystalline precipitates insoluble in water. When heated with sodium acetate and acetic anhydride, it yields 2-*nitro*-4'-*acetamidonaphthaphenazine*, which crystallises from nitrobenzene in orange-yellow needles insoluble in water, but dissolving in alcohol to a yellow solution with a green fluorescence. When hydrolysed with sulphuric acid, it yields 4'-*amido*-2-*nitromethylnaphthaphenazonium sulphate*, as a blood-red precipitate, from which, by removal of the amido-group 2-*nitromethylnaphthaphenazonium* may be obtained. The *chloride*, $\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{Cl}$, of the latter compound crystallises in orange-yellow plates which are readily soluble in alcohol or hot water, the alcoholic solution exhibiting a yellow fluorescence; the *nitrate*, which is insoluble in dilute nitric acid, crystallises in glistening, golden plates. 2-*Amidomethylnaphthaphenazonium chloride*, $\text{C}_{17}\text{H}_{14}\text{N}_3\text{Cl}$, obtained by the reduction of the nitro-compound with stannous chloride and hydro-

chloric acid, crystallises in dark violet, almost black, glistening needles, and is readily soluble in alcohol or water, but its solutions are not fluorescent. The *aurichloride, platinochloride, nitrate, acetyl* derivative, and *platinochloride* of the acetyl derivative have been prepared.

<div align="right">J. J. S.</div>

The Sixth Isomeride of Rosinduline. By FRIEDRICH KEHRMANN, and ALBERT LEVY (*Ber.*, 1898, **31**, 3097—3106).—2-*Nitrophenyliso-naphthaphenazonium ferrichloride*, $C_{22}H_{14}N_3O_2FeCl_4$, is obtained by condensing nitrophenylorthophenylenediamine sulphate with β-naphthaquinone and pouring the product into ferric chloride solution ; it cannot be crystallised without undergoing decomposition. The *nitrate*, $C_{22}H_{14}N_3O_2 \cdot NO_3$, crystallises in pale red needles, and the *platinochloride*, $(C_{22}H_{14}N_3O_2)_2PtCl_6$, forms a yellowish-red, crystalline powder insoluble in water.

2-*Acetamidophenylisonaphthaphenazonium chloride*, $C_{24}H_{18}N_3OCl$, obtained when the iron double salt is reduced with stannous chloride and hydrochloric acid, and the crude product heated with acetic anhydride and sodium acetate, forms small, yellowish-red crystals and dissolves in hot water or alcohol, yielding non-fluorescent solutions. The *platinochloride* and *dichromate*, $(C_{24}H_{18}N_3O)_2Cr_2O_7$, are both insoluble in water.

2-*Amidophenylisonaphthaphenazonium bromide*, $C_{22}H_{16}N_3Br$, forms black crystals with a bronzy lustre, and is readily soluble in alcohol or water, yielding violet solutions. The *platinochloride*, $(C_{22}H_{16}N_3)_2PtCl_6$, crystallises in bluish-black needles. Amines readily react with the salts of this new isomeride of rosinduline, as the para-position to the azine nitrogen is free. The amine residue which is thus introduced takes the ortho-position relatively to the amido-group already present, and orthodiamines are thus obtained which can be converted into fluorindine compounds.   3-*Dimethylamido*-2-*amidophenylisonaphthaphenazonium nitrate*, $C_{24}H_{21}N_4 \cdot NO_3 + H_2O$, obtained by the action of dimethylaniline on the " tin double salt " of the isorosinduline suspended in alcohol, and by subsequent treatment with potassium nitrate, crystallises from water in green, glistening needles; it dissolves in water or alcohol, yielding magenta-coloured solutions. The *chloride*, which is readily soluble in water, and the *platinochloride* and *dichromate*, both of which are sparingly soluble, have also been prepared.

3-*Anilido*-2-*amidophenylisonaphthaphenazonium chloride*, $C_{28}H_{21}N_4Cl$, obtained by the action of aniline on the " tin double salt," forms bronzy, glistening crystals.   Diethylamine reacts with the " tin double salt," yielding 2-*amidoisorosindone*, $O{<}{\begin{smallmatrix} N Ph ———·— C_{10}H_6 \\ C_6H_3(NH_2){:}N \end{smallmatrix}}$, which crystallises from alcohol or benzene in yellowish-red plates melting above 300°. Acetylisorosinduline chloride, when treated with dimethylamine in slight excess, yields *acetamidoisorosindone*, which, on hydrolysis with 50 per cent. sulphuric acid, yields amidoisorosindone, and from this, by removal of the amido-group, *isorosindone*, $C_{22}H_{14}N_2O$, the third and last theoretically possible isomeride of rosindone, is obtained.   It crystallises from benzene in reddish-violet plates with a coppery lustre, and melts at 267° ; it is insoluble in water or alkalis, but

dissolves in alcohol, ether, acetic acid, or benzene, yielding violet-red solutions ; the alcoholic solution exhibits a faint red fluorescence.

The green 2-nitro-4'-amidophenylisonaphthaphenazonium described in the preceding abstract may be converted into 2-amidophenyliso-naphthaphenazonium (see above) by eliminating the amido-group, and then reducing the nitro-compound. The same nitramido-compound (either brown or green modification), when reduced with stannous chloride, yields 2 : 4'-*diamidophenylisonaphthaphenazonium chloride* as bronzy, lustrous crystals. It is an extremely strong base, as both amido-groups are in the para-position relatively to azonium nitrogen, and yields an insoluble *platinochloride.*   J. J. S.

Condensation Products from Flavinduline and Deoxybenzoin. By FRANZ SACHS (*Ber.*, 1898, **31**, 3073—3075).—Flavinduline (*Annalen*, 1896, **292**, 266), as a type of the azonium bases, readily reacts with methylene compounds, yielding characteristic colorations. When an alcoholic solution of the azonium chloride and an equivalent quantity of any of the following compounds is treated with potassium hydroxide, even in the cold, an intense green coloration is developed ; ethylic acetoacetate and its substituted derivatives, ethylic cyanacetate, ethylic malonate, malononitrile, acetylacetone, phloroglucinol, resorcinol, benzylic cyanide, and deoxybenzoin. The condensation product with deoxybenzoin has been more closely examined ; a solution of 2 grams of deoxybenzoin in alcohol is added to a solution of 4·4 grams of commercial flavinduline (containing 13 per cent. of ash) in 300 c.c. of alcohol, and the mixture treated with the theoretical quantity of sodium hydroxide solution, and heated to the boiling point of the alcohol. When quickly cooled and allowed to remain for 24 hours, dark coloured crystals of a *compound*, $C_{40}H_{28}N_2O_2$, similar in appearance to potassium permanganate, are obtained ; this is insoluble in water or light petroleum, sparingly soluble in alcohol, more readily in acetone, ether, or ethylic acetate, and readily in toluene, benzene, chloroform, carbon tetrachloride, carbon bisulphide, or methylal. Most of its solutions are green or bluish-green ; its alcoholic solution, when treated with a few drops of hydrochloric acid, yields an intense blue solution of a salt, but when this solution is boiled, it changes to an orange-red colour ; the latter can also be obtained by passing dry hydrogen chloride into a solution of the base in toluene. Apparently, two isomeric salts exist in the two coloured solutions. The orange-red salt yields a *platinochloride,* $(C_{40}H_{27}N_2O_2)PtCl_6$. It is probable that the two different colours are due to the presence of two different chromophore groups of the ortho- and para-quinone types.

J. J. S.

Compounds containing a previously unknown Ring. By MILORAD Z. JOVITSCHITSCH (*Ber.*, 1898, **31**, 3036).—The compound,

$$\text{COOEt·CH–N—O}$$
$$\text{NPh·N—O}$$
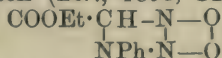
(Abstr., 1898, i, 93), has the normal molecular weight. The product of hydrolysis is most likely a mixture.

M. O. F.

Products of the Action of Sulphur on Dimethylaniline. By RICHARD MÖHLAU and VOLKMAR KLOPFER (*Ber.*, 1898, **31**, 3164—3166. Compare Abstr., 1888, 364)—The compound $C_8H_7NS_2$, which was previously found to be the primary product of the action of sulphur on dimethylaniline, melts at 88—89°, boils at 335°, and yields a *platinochloride*, $(C_8H_7NS_2)_2,H_2PtCl_6$, which crystallises in yellowish-red prisms. It is not attacked by hydriodic acid, but is converted by nitric acid into *iso-μ-methylbenzothiazole*, $CH_2{<}^{N-C_6H_4}_{CH\cdot S}$, which crystallises in compact plates, melts at 202°, and yields a *platinochloride* crystallising in yellow tablets. The base, when heated with sulphur, is converted into benzothiazole. All these reactions point to the formula $^{CH_2\cdot N-C_6H_4}_{S-CH\cdot S}$ as the most probable for the original compound.　　　　　　　　　　　　　　　　　　　A. H.

Composition of Diuretin. By ABA VON SZTANKAY (*Chem. Centr.*, 1898, i, 1281—1282; from *Pharm. Post.*, **31**, 189—190 and 201—202).— Diuretin is said to be a double compound of the sodium compound of theobromine with sodium salicylate; it is a homogeneous substance, for it can be precipitated unchanged by means of alcohol. The unpleasant effects caused by a dose of diuretin led the author to suspect that the sodium theobromine compound is not a simple derivative of dimethylxanthine, obtained by replacing the hydrogen atom by an atom of sodium, and the analysis of the compound prepared by the action of sodium ethoxide on theobromine corresponded with a composition $C_7H_8N_4O_2,NaOH$. Moreover, in three experiments, from 1·3 grams of theobromine, 0·23 of sodium, and 1·6 of anhydrous sodium salicylate, 3·807, 3·807, and 3·806 grams of diuretin were obtained respectively. This increase of weight, according to the author, cannot be ascribed to any hygroscopic character of the substance, but indicates a composition

$$C_7H_8N_4O_2,NaOH,OH\cdot C_6H_4\cdot COONa.$$
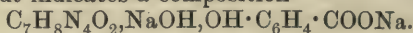
　　　　　　　　　　　　　　　　　　　　　　　　E. W. W.

Active Principles of Certain Aroids. By ALEXANDRE HÉBERT and F. HEIM (*Bull. Soc. Chim.*, 1898, [iii], **17**, 664—669).—Examinations of extracts obtained from *Arum maculatum* and *A. italicum*, *Arisarum vulgare*, *Amorphophallus Rivieri*, and *Caladium bulbosum* have demonstrated the presence of an acid saponine and a volatile, liquid alkaloid; the latter was obtained as a brown, unstable liquid, having a sharp taste and an odour of mice; it is sparingly soluble in water, but dissolves in alcohol, benzene, amylic alcohol, chloroform, ether, and petroleum, fumes in presence of hydrogen chloride and gives a hydrochloride which is soluble in alcohol. The properties of the base closely resemble those of coniine, but its toxic power is apparently more feeble than in the case of that alkaloid. No appreciable quantity of hydrogen cyanide could be obtained from any portion of the above aroids.　　　　　　　　　　　　　A. L.

Organic Chemistry.

Action of Acetylene on Metal Ammoniums. By HENRI MOISSAN (*Compt. rend.*, 1898, **127**, 911—917).—When ammonia is liquefied in contact with sodium, potassium, lithium, and calcium, and acetylene is passed into the liquid, cooled at − 40° to − 80°, the deep blue colour gradually disappears, and a colourless liquid is obtained, ethylene being liberated when the temperature is allowed to rise. When the colourless liquid is strongly cooled, or when the ammonia is allowed to volatilise, a white, crystalline solid is obtained. Sodium yields the compound C_2HNa in microscopic, rhombohedral lamellæ. The author considers that it is more accurately represented by the formula C_2Na_2,C_2H_2; if it is suspended in benzene, and iodine is added until a permanent coloration is obtained, the insoluble residue consists of the carbide C_2Na_2, and contains no sodium iodide, whilst the benzene contains carbon iodide. Potassium yields the analogous compound C_2K_2,C_2H_2, which crystallises readily in brilliant, silky, rhombohedral lamellæ.

Lithium yields rhombohedra of the compound $C_2Li_2,C_2H_2,2NH_3$, which becomes incandescent in contact with water or when thrown into chlorine; it also takes fire in contact with carbonic anhydride or sulphurous anhydride.

Calcium yields transparent prisms of the compound $C_2Ca,C_2H_2,4NH_3$, which also becomes incandescent in contact with water, chlorine, carbonic anhydride, or sulphurous anhydride.

All these compounds dissociate when heated, and yield the carbides C_2Na_2, C_2K_2, C_2Li_2, and C_2Ca respectively.   C. H. B.

Action of Chlorine on Acetylenic Tetrabromide in the Presence of Aluminium Chloride. By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1897, [iii], **17**, 799—801).—When a mixture of acetylenic tetrabromide (100 grams) with anhydrous aluminium chloride (30 grams) is heated at 70—80° in a reflux apparatus, there is a slow, but distinct, liberation of hydrogen chloride, and on passing chlorine into the mixture, much hydrogen chloride and large quantities of bromine are evolved. From the solid product of the reaction, hexachlorethane was isolated. The same compound is formed by the action of chlorine on ethylenic bromide in the presence of aluminium chloride.

N. L.

Action of Chlorine on Pentachlorethane in Presence of Aluminium Chloride. By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1897, [iii], **17**, 797—799).—No reaction occurs when chlorine is passed into pentachlorethane, heated at 70° in a reflux apparatus and exposed to diffused light, but on adding aluminium chloride, the gas is completely absorbed, there is an abundant evolution of hydrogen chloride, and hexachlorethane is formed in almost theoretical quantity. When pentachlorethane is heated at 70° with aluminium chloride alone, there is a decided evolution of hydrogen chloride, together with the forma-

tion, it is suggested, of a compound of the formula $CCl_3 \cdot CCl_2 \cdot AlCl_2$, which is converted by the action of chlorine into hexachlorethane, with regeneration of aluminium chloride.   N. L.

The Sugar of Diabetic Urine. By LE GOFF (*Compt. rend.*, 1898, **127**, 817—819).—The sugar was isolated in a pure state by evaporating the urine in a vacuum, separating the crystals formed by filtration, washing with cold alcohol of 90° in order to remove urea, colouring matter, and chlorides, and finally crystallising several times from boiling alcohol of 95°. The crystals thus obtained had the composition $C_6H_{12}O_6 + H_2O$, but on standing lost the greater part of their water of crystallisation; the sugar was easily fermented by yeast, reduced Fehling's solution, and had $[a]_D = 49 \cdot 46$ when dissolved as $C_6H_{12}O_6 + \frac{1}{2}H_2O$. Its osazone melted at 230°; *d*-glucosazone, according to G. Bertrand, melts at the same temperature, and not at 204—205° as stated by Fischer. On oxidation, the sugar gave rise to *d*-gluconic acid, which was characterised by the rotatory power of its calcium salt; from this and the foregoing properties, the sugar isolated appears to be identical with *d*-glucose, a result which is in accord with the views generally held.   W. A. D.

Action of Potash on Oxynitrocellulose. By LÉO VIGNON (*Compt. rend.*, 1898, **127**, 872—874).—Oxynitrocellulose, prepared by the method previously described by the author (Abstr., 1898, i, 8), dissolves in aqueous caustic potash (sp. gr. = 1·162) with considerable development of heat, giving a brown solution; little gas is evolved. On neutralising the product with acetic acid at 0°, and subsequently passing hydrogen sulphide during 2 hours at the ordinary temperature, oxides of nitrogen are evolved and sulphur deposited; after warming on the water-bath to expel dissolved gases, and subsequently cooling, 20 c.c. of a solution containing 12 grams of phenylhydrazine and 7·5 grams of glacial acetic acid in 100 c.c. of water is added, when a crystalline precipitate separates, especially if the solution is warmed at 80° for 20 minutes; on recrystallising the product from toluene, light yellow prisms are obtained which melt and decompose at 204°, and probably consist of the osazone of Will's hydroxypyruvic acid, $OH \cdot CH_2 \cdot CO \cdot COOH$, obtained by acting with potash on collodion (Abstr., 1891, 542, and 1892, 356).

If a C_6-formula be assumed, oxycellulose, from its properties, appears to be a trihydric alcohol, possessing certain aldehydic and acid functions (compare Abstr., 1898, i, 8). The structure

$$\left\{ \begin{matrix} CH_2 \diagup C \cdot - CH(OH) \diagdown \\ \quad | \quad O \diagup \qquad \qquad \diagup CH \cdot OH \\ O - \diagdown CH \cdot CH(OH) \diagup \end{matrix} \right\}_n$$
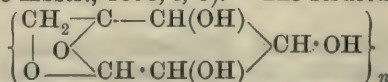
is provisionally assigned to cellulose, whilst the oxycelluloses appear to contain n cellulose nuclei combined with the group

$$CHO \cdot (CH \cdot OH)_3 \cdot CH {<}^{CO}_{\ O},$$
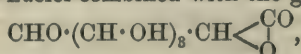
characteristic of oxycellulose; on hydration, the latter group is transformed into the acid $CHO \cdot (CH \cdot OH)_4 \cdot COOH$, which is capable of undergoing further change in two different ways according to the

equations (1) $C_6H_{10}O_7 = CO_2 + 3H_2O + C_5H_4O_2$, furfuraldehyde being formed, or (2) $C_6H_{10}O_7 + O_2 = 2C_3H_4O_4 + H_2O$, in which case hydroxy-pyruvic acid is produced. The formation of the latter from oxy-nitrocellulose is thus explained if it be assumed that the NO_3 groups present serve as a means of supplying the oxygen required by the second of the above equations. W. A. D.

Action of Hydrocyanic Acid on Epichlorhydrin. By ROBERT LESPIEAU (*Compt. rend.*, 1898, **127**, 965—966).—When 150 grams of epichlorhydrin are heated with 70 grams of pure hydrogen cyanide in a sealed tube at 60° for 60 hours, a yellowish liquid is obtained which has the composition C_4H_6ClON, and boils at 110—111° under a pressure of 2 mm., and at about 140° under a pressure of 15 to 20 mm. When dissolved in ethylic alcohol and heated with hydrogen chloride, it yields an ethereal salt, $C_6H_{11}ClO_3$, which boils at 121—122° under a pressure of 14 mm.

The nitrile probably has the constitution $CH_2Cl\cdot CH(OH)\cdot CH_2\cdot CN$.
C. H. B.

Non-explosive Decomposition, and Determination of the Stability of Gun-cotton. By C. HOITSEMA (*Zeit. physikal. Chem.*, 1898, **27**, 567—578).—The author has previously shown that, with some compounds, rapid and slow decomposition yield identical products, whilst for others the reverse obtains (Abstr., 1897, ii, 17); gun-cotton belongs to the latter class, so that no explosion-velocity experiments are possible. At about 150°, it can be slowly decomposed without explosion, evolving gases containing a little nitric peroxide, and leaving a non-explosive, peat-like mass containing about 7 per cent. of nitrogen. The formation of higher oxides of nitrogen does not appear to be due to secondary reactions, as, by means of apparatus described, it is proved to precede the formation of nitric oxide. It seems more probable, therefore, that the higher oxides are due to impurity, or are produced merely in the initial stages of the reaction. The usual method for the determination of the stability of gun-cotton is the observation of the time which elapses before nitric fumes are evolved when the sample is kept at a certain fixed temperature. In the apparatus described, the explosive may be maintained for any length of time at any desired temperature, and the author considers a better method of determining the stability to consist in ascertaining the highest temperature at which the sample may be kept for a quarter of an hour, or some such time, without the production of nitric fumes.
L. M. J.

Action of Oxidising Agents on Nitrogenous Compounds. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1898, **127**, 1028—1030. Compare Abstr., 1898, i, 548, 564, and 566).—The author has investigated the action of concentrated solutions of chromic acid and potassium dichromate on solutions of amines and amides. Hydroxylamine is at once decomposed with the evolution of nitrogen and nitrous fumes. Phenylhydrazine and methylphenylhydrazine yield nitrogen, and, when the action is aided by heat, a small amount of phenol is produced. Urethane is attacked by warm chromic acid, but is not affected by dichromate. Acetamide is only partially de-

composed by warm chromic acid, but if warmed with an alkaline solution of potassium chromate, a considerable quantity of nitrogen is evolved ; benzamide under these conditions is scarcely affected. Carbamide is oxidised by warm solutions of the above reagents, but less energetically than by alkali hypochlorites. Thiocarbamide is very stable towards these agents ; the decomposition is partial, and a mixture of carbonic anhydride and nitrogen in molecular proportion is evolved. Phenylthiocarbamide is not attacked by dichromate, but is oxidised by chromic acid, carbonic anhydride (1 mol.) being liberated. The hydrochlorides of methylamine and ethylamine are decomposed, giving rise to chlorine, nitrogen, and carbonic anhydride, together with a small quantity of free oxygen (see next abstract). G. T. M.

Action of Oxidising Agents on Fatty and Aromatic Amines. By WILLIAM OECHSNER DE CONINCK and A. COMBE (*Compt. rend.*, 1898, 127, 1221—1223).—When strong, aqueous solutions of chromic acid in potassium dichromate are warmed with the hydrochlorides of methylamine and ethylamine, very little action takes place ; in presence of a little dilute sulphuric acid, however, gradual decomposition occurs, and carbonic anhydride, chlorine, and nitrogen are evolved. Even ammonium chloride is decomposed by a very strong solution of the oxidising mixture.

The hydrochlorides of aniline, ortho- and para-toluidines, diphenylamine, the phenylenediamines and rosaniline yield large quantities of carbonic anhydride, and aromatic amines in general yield colouring matters in addition. Benzylamine gives carbonic anhydride and a notable quantity of benzaldehyde. Piperidine is slowly attacked by the warm mixture, being more stable than the aromatic amines in this respect. A. L.

Salts of Perchromic Acid. By O. FRITZ WIEDE (*Ber.*, 1898, 31, 3139—3143. Compare Abstr., 1898, ii, 28, 295).—These salts were obtained by adding a small quantity of the base to an ethereal solution of perchromic acid cooled below 0°, and drying the crystals on a porous plate ; the tetramethylammonium hydroxide had to be added in aqueous solution, of course, but the water was removed from the mixture in the form of ice ; in the preparation of the quinoline compound, the ethereal solution of perchromic acid was diluted with an equal volume of light petroleum, when the water dissolved in the ether solidified. None of the compounds now described crystallised with a molecule of hydrogen peroxide.

Tetramethylammonium perchromate, CrO_5NMe_4, forms a brownish-violet, crystalline powder ; in the cold, it loses oxygen slowly, leaving the dichromate ; when it is heated, oxygen is first evolved with a hissing noise, and then the yellow dichromate left burns, sending out a shower of sparks. When the salt is mixed with solutions of silver nitrate or barium chloride, the oxides of these metals are formed, from which it may be inferred that their perchromates are incapable of existence.

Trimethylammonium perchromate is dark-coloured ; it is spontaneously explosive, unlike either the ammonium or tetramethylammon-

ium salt. *Quinoline perchromate*, CrO_5H,NC_9H_7, is blue and unstable; it explodes slightly when heated. *Piperidine perchromate*, CrO_5H,NC_5H_{11}, is dark violet in colour, and very soluble in water; it explodes when heated. C. F. B.

Active Methylbutylenediamine (2-Methyl-1 : 4-diaminobutane). By L. ETAIX and PAUL FREUNDLER (*Bull. Soc. Chim.*, 1897, [iii], **17**, 805—808).—The ethereal salts of β-methyladipic acid form an exception to the law of the product of asymmetry, and it therefore seemed of interest to ascertain whether a reduction in the length of the chains attached to the asymmetric carbon atom would be accompanied by an increase in the rotatory power, a change the reverse of that which occurs when the attached groups are lengthened. For this purpose, ethylic β-methyladipate was converted into methylbutylenediamine through the hydrazide and azide, according to Curtius' method. The ethylic salt employed had a rotatory power $[a]_D = +3°$, and was prepared from the menthone obtained by the action of dilute sulphuric acid on menthol.

β-Methyladipic hydrazide, $N_2H_3 \cdot CO \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CO \cdot N_2H_3$, obtained by heating a mixture of ethylic β-methyladipate (75 grams) with fuming hydrazine hydrate (55 grams) for 6 hours at 150—170°, crystallises in colourless needles melting at 136°, and is soluble in water, boiling alcohol, and acetone, but almost insoluble in cold alcohol and in other organic solvents. *β-Methyladipic azide*, $C_5H_{12}(CO \cdot N_3)_2$, prepared by adding sodium nitrite (3 mols.) to a solution of the hydrazide in 10 times its weight of water at 0°, is a heavy, brownish oil which does not solidify at $-10°$; it cannot be completely purified, owing to its rapid decomposition at the ordinary temperature. The azide is heated for some time with absolute alcohol in a reflux apparatus, and the mixture of the urethane with the corresponding carbamic acid which is thus obtained is heated in sealed tubes at 130—150° with concentrated hydrochloric acid; the contents of the tubes are then filtered, saturated with solid caustic potash, and the methylbutylenediamine extracted with ether and purified by distillation.

Active methylbutylenediamine, $NH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot NH_2$, is a mobile, fuming liquid of fœtid odour, boiling at 170°; its specific rotatory power is $[a]_D = +30·5°$. The *hydrochloride* crystallises in small prisms soluble in water and alcohol; the *platinochloride* in orange scales melting and decomposing at 200°; the *picrate* in small, yellow needles decomposing at about 180°. The *dibenzoyl* derivative crystallises in colourless needles melting at 151—152°, and is soluble in alcohol, but insoluble in water.

As was anticipated, the rotatory power of methylbutylenediamine is greater than that of ethylic methyladipate. It is somewhat remarkable that the rotatory power of the latter was not destroyed by the successive operations to which it was subjected, and it is inferred that racemisation depends, not on the agents of transformation, but on the nature of the groups attached to the asymmetric carbon atom. Active substances in which these groups are hydrocarbon radicles, or are attached by means of intermediate hydrocarbon residues, appear to possess a special degree of stability. N. L.

Glucosamine [Chitosamine] Hydrochloride. By CHARLES TANRET (*Bull. Soc. Chim.*, 1897, [iii], 17, 802—805).—Glucosamine hydrochloride exhibits the phenomenon of birotation, and should, therefore, exist in two modifications. The α-variety has the higher rotatory power, and is the ordinary salt obtained by crystallisation from water, whilst the more stable β-variety, of lower rotatory power, has hitherto been known only in solution. A number of determinations of the rotatory power of solutions of the β-modification, obtained by heating solutions of ordinary glucosamine hydrochloride, or by allowing them to remain for 1 or 2 days, gave $+72.5°$ as the value of $[\alpha]_D$, a result which is appreciably higher than those obtained by Ledderhose, Tiemann, and Hoppe-Seyler. This difference is, in all probability, due to excessive heating of the solutions employed by those observers, for it was found that the rotatory power of a 10 per cent. solution was reduced to $70.8°$ by 14 minutes heating in the water-bath, and to $70.0°$ after 28 minutes. The value of $[\alpha]_D$ for α-glucosamine hydrochloride was found to be $+100°$, the solution being prepared and the determination made within 4 minutes at 20°.

β-Glucosamine hydrochloride was obtained in the form of microscopic crystals by pouring a concentrated solution, prepared at 60°, into 10 times its weight of absolute alcohol. When dissolved in water and quickly examined, the rotatory power was found to be $+75°$, but after some hours it fell to $72.5°$ owing to the re-formation of the α-variety. The two modifications of glucosamine hydrochloride, specimens of which were examined by Wyrouboff, crystallise in different systems, the α-variety in the monoclinic, and the β-variety in the hexagonal, system. N. L.

Glucosines. By CHARLES TANRET (*Bull. Soc. Chim.*, 1897, [iii], 17, 801—802).—The discrepancies between the author's results and those obtained by Brandes and Stoehr (Abstr., 1897, i, 230) in the examination of α- and β-glucosine are due to essential differences in the methods by which the bases were obtained. N. L.

Valency of Boron. By Sir EDWARD FRANKLAND (*Compt. rend.*, 1898, 127, 798—799).—In discussing the structure of the substance $NaB(OEt)_4$, which Copaux has adduced as the first certain proof of the pentad nature of boron (this vol., i, 183), the author points out that in ascribing formulæ to ammonia-borontrimethyl, $H_3N:BMe_3$, and to the substance $B(OEt)_3:BEt(OEt)_2$ (Abstr., 1876, 618), he also has previously assumed boron to be pentad. Both these compounds dissociate, however, when distilled, although their constituents recombine on cooling; in this respect, they resemble ammonium chloride, and consequently the objections which can be raised against the pentad nature of nitrogen are also valid in the case of boron. From the fact that ethylic iodide at 140° does not interact with the compound described by Copaux, the author considers that the formula $ONa \cdot BEt(OEt)_3$ should be given to the latter, rather than that assigned to it by the discoverer. W. A. D.

Action of Oxygen on Solutions of Formaldehyde. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1897, [iii], 17, 938—940).—Oxygen is without action on aqueous solutions of formaldehyde at

ordinary temperatures, but is rapidly absorbed at 200°. In presence of caustic potash, there is no absorption of oxygen at temperatures below 100°, but in the course of a month at ordinary temperatures complete transformation of the aldehyde into formate and methylic alcohol occurs; in presence of platinum sponge, however, the supernatant oxygen is slowly replaced by an equal bulk of carbonic anhydride, in accordance with the equation $CH_2O + O_2 = CO_2 + H_2O$, and this change goes on equally rapidly in darkness or on exposure to light. A. L.

Action of Bromine on Chloral in the Presence of Aluminium Chloride. By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1897, [iii], **17**, 796—797).—Two hundred and fifty grams of finely powdered anhydrous aluminium chloride was dissolved in 500 grams of chloral, the liquid heated to 75—80°, and bromine gradually added until it was no longer absorbed. On pouring the mixture into dilute aqueous soda, a substance was precipitated which proved to be hexachlorethane. This compound is also the product of the action of iodine on chloral in the presence of aluminium chloride. N. L.

Aliphatic Aldazine Derivatives and their Products of Rearrangement. By ADOLF FRANKE (*J. pr. Chem.*, 1898, [ii], **58**, 464).—With reference to the work of Curtius and Zinkeisen (this vol., i, 165), the author points out that he had already prepared the aldazine of isobutyraldehyde from hydrazine hydrate and isobutyraldol (*Monatsh.*, 17, 643, 672). This aldazine gives a beautifully crystalline hydrochloride, which, when treated with caustic potash, yields, not the aldazine, but an isomeric substance smelling strongly of camphor. It is probably produced by rearrangement and closing of the ring. The author proposes to further study this point. A. W. C.

History of Citral. By FERDINAND TIEMANN (*Ber.*, 1898, **31**, 3278—3296).—The author gives a *résumé* of the more important researches on citral. J. J. S.

Hydrosulphonic Acid Derivatives of Cinnamaldehyde, of Citronellal, and of Citral. By FERDINAND TIEMANN (*Ber.*, 1898, **31**, 3297—3324).—[With PAUL KRÜGER.]—Heusler's work (Abstr., 1891, 1052) on the hydrosulphonic derivatives of cinnamaldehyde has been repeated, and the results confirmed. The addition of sulphurous acid to an unsaturated compound takes place more readily when a normal instead of an acid sulphite is employed, provided the alkali which is formed during the reaction is neutralised by a bicarbonate or by carbonic anhydride. When cinnamaldehyde is covered with a 20—25 per cent. solution of sodium sulphite, and carbonic anhydride is bubbled through the mixture, the whole of the aldehyde, with the exception of small quantities of impurities, goes into solution; similar results are obtained when the aldehyde (1 mol.) is shaken with a solution of sodium sulphite (2 mols.) and sodium hydrogen carbonate (2 mols.). If the aldehyde solution is then covered with ether and shaken with an excess of sodium hydroxide, 75 per cent. of the aldehyde is recovered, and on warming and again extracting with ether, a further quantity of aldehyde is obtained, but in no case more

than 80 per cent. It is thought probable that two isomeric sulphonic acids, $SO_3H \cdot CHPh \cdot CH_2 \cdot COH$ and $CH_2Ph \cdot CH(SO_3H) \cdot COH$, may be formed, one of which is more readily decomposed than the other.

Sulphurous anhydride reacts with citronellal in a somewhat violent manner, pulegone and its hydrosulphonic acids being formed, which then yield terpenes and polyterpenes. The normal citronellal sodium hydrogen sulphite additive compound,

$$CMe_2 \text{:} CH \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CH(OH) \cdot SO_3Na,$$
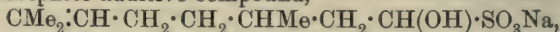
obtained by shaking an ice cold solution of sodium hydrogen sulphite (free from anhydride) with the aldehyde, is readily soluble in water, but may be separated by adding saturated sodium chloride solution; it is completely decomposed at the ordinary temperature by sodium carbonate or sodium hydroxide. That the elements of sodium hydrogen sulphite are attached to the aldehyde group is proved by the fact that the additive compound, when treated with phenylhydrazine acetate, yields citronellal phenylhydrazone, and with semicarbazide hydrochloride yields *citronellal semicarbazone,*

$$C_9H_{17} \cdot CH \text{:} N \cdot NH \cdot CO \cdot NH_2,$$
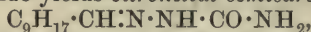
in the form of plates melting at 84°. A *dihydrosulphonic acid,* $SO_3Na \cdot C_9H_{18} \cdot CH(OH) \cdot SO_3Na$, is obtained when the aldehyde or the above-mentioned additive product is treated with a sufficient quantity of warm, sodium hydrogen sulphite solution containing sodium sulphite. When warmed with dilute sodium hydroxide, the disulphonic acid yields the sodium salt of a *monhydrosulphonic acid,* $SO_3 \cdot C_9H_{18} \cdot COH$, which is not decomposed by boiling with sodium hydroxide solution. Its constitution must be either

$$SO_3H \cdot CMe_2 \cdot [CH_2]_3 \cdot CHMe \cdot CH_2 \cdot COH$$
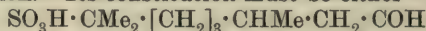
or $CHMe_2 \cdot CH(SO_3H) \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot COH$.

[With GEORG LEMME.]—Specimens of citral, obtained by five different methods, all exhibited the same properties, and gave identical derivatives. The normal additive compound of citral and sodium hydrogen sulphite is obtained when citral (100 parts), $Na_2S_2O_3 + 7H_2O$ (100 parts), water (200 parts), and acetic acid (25 parts) are well shaken; it is decomposed on dissolving it in water, but may be recrystallised from methylic alcohol containing a little acetic acid; a theoretical yield of citral can never be obtained from the compound. Citryl-β-naphthacinchonic acid melts at 199—200°. A *stable dihydrosulphonic acid* derivative of citral is obtained when the normal compound is subjected to steam distillation or is boiled with chloroform, half the citral being regenerated; it readily reacts with phenylhydrazine, but a pure phenylhydrazone has not been obtained, neither has the constitution as yet been settled. A *labile dihydrosulphonic acid* is obtained when citral is shaken with sodium sulphite, and the sodium hydroxide which is set free is neutralised. It is readily soluble in water, and is decomposed by an excess of alkali. It may be shown to contain the aldehyde group, since it reacts with semicarbazide, yielding *sodium citralsemicarbazonedihydrodisulphonate.* A detailed description of the method for the preparation of this labile disulphonic acid is given, and also a method by means of which citral may be titrated with sulphuric acid and sodium sulphite. When the disulphonic acid

is evaporated in the presence of a small quantity of alkali, it loses the elements of sodium sulphite, and unaltered citral is regenerated ; in purifying citral, it suffices to form the labile disulphonic compound in solution, and then decompose with alkali. The labile compound is moderately stable in the presence of acids, but by prolonged action becomes converted into the isomeric stable compound. *Sodium citral-hydrosulphonate*, obtained when the labile dihydrodisulphonate is shaken with citral, is more readily soluble in methylic alcohol than the sodium salt of the disulphonate, and is immediately decomposed by sodium hydroxide. J. J. S.

Detection and Estimation of Citral. By FERDINAND TIEMANN (*Ber.*, 1898, **31**, 3324—3340).—In the Doebner citral test (Abstr., 1894, i, 262, 532), in addition to citryl-β-naphthacinchonic acid (m. p. 310°), two other products are also formed, namely, a-methyl-β-napthacinchonic acid and the *β-naphthalide* of *methylnaphtha-cinchonic acid* melting at 230—232°. The amount of citryl naphtha-cinchonic acid is usually about 46 per cent. of the theoretical ; the acid crystallises in a pure state when sufficient citral is present, but other-wise methyl-β-naphthacinchonic acid also crystallises with it. It follows that Doebner's reaction is an extremely good test for citral, but the presence of products of higher melting point cannot be taken to indicate the presence of another aldehyde. Oils containing citral yield some 80—85 per cent. of their citral in the form of the cinchonic acid, but with oils containing only small quantities of citral, the above-mentioned products of higher melting point are formed, and the method can no longer be used as a quantitative process. The detec-tion of citronellal in the presence of citral can only be depended on when 10 per cent. at least of the former is present.

Citralidenecyanacetic acid, $C_9H_{15}\cdot CH\!:\!C(CN)\cdot COOH$, obtained when cyanacetic acid is shaken with citral in the presence of aqueous sodium hydroxide, separates, on acidifying, as an oil which rapidly solidifies ; in the crude form, it melts at 85—90°, but, after recrystal-lisation from benzene, at 122°. About 92—95 per cent. of the theoretical quantity of the crude acid is obtained, and citral in various oils may be estimated by this method.

When treated in the usual manner with semicarbazide, citral gives a mixture of two semicarbazones, of which one, crystallising in needles and melting at 164°, is first deposited, the amount being some 60—70 per cent. ; the aqueous mother liquor contains a second semicarbazone crystallising in plates and melting at 171°. A mixture of the com-pound of low melting point with some 6—10 per cent. of the other melts at 135°, the melting point of the crude citral semicarbazone. The semicarbazones cannot be employed as a basis for a method for estimating citral.

According to the author, the best methods for estimating citral are : (1) conversion into citralidenecyanacetic acid ; (2) conversion into the normal sodium hydrogen sulphite derivative ; (3) conversion into the labile sodium citraldihydrodisulphonate (see preceding abstract). The other constituents of lemon grass and similar oils, for example, ger-aniol, linalool, and hydrocarbons, do not appear to combine with sodium

hydrogen sulphite. The sulphite method is employed by Schimmel and Co. for estimating cinnamaldehyde in oil of Cassia and citral in lemon grass oil.   J. J. S.

Action of Alkaline and Acid Reagents on Citral. By FERDINAND TIEMANN (*Ber.*, 1899, **32**, 107—115).—Citral,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CHO,$$
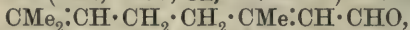
is converted by acids into cymene, and this reaction probably proceeds in several stages, the elements of water being first assumed and then again lost; even on this assumption, it must be supposed that one of the double linkings migrates from a position in one of the side chains into the benzene ring. The first product of the action of acids probably has the constitution $OH{\cdot}CMe{<}^{CH_2\underline{\qquad}CH_2}_{CH_2{\cdot}CH(OH)}{>}CH{\cdot}CMe_2{\cdot}OH$, and is converted by loss of the elements of water into a compound of the formula $CMe{<}^{CH{\cdot}CH_2}_{CH:CH}{>}C{:}CMe_2$, which then passes into cymene by the migration of the double linking. Unsuccessful attempts have been made by the author to bring about a migration of one of the double linkings of citral without the formation of a benzene ring. Acids such as sulphurous acid, and sulphuric acid in presence of an oxidising agent, acting on an excess of citral, fail to produce any isomeric compound, cymene, resinous products, and unaltered citral being the result of all these reactions. Caustic soda causes a partial decomposition into methylheptenone and acetaldehyde, and also produces resinous substances, but does not bring about the formation of an isomeride.   A. H.
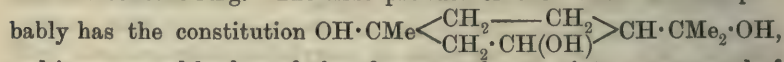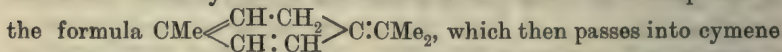
Action of Semicarbazide on Samples of Citral Purified by Different Methods. By FERDINAND TIEMANN (*Ber.*, 1899, **32**, 115—121. Compare preceding abstracts).—Ordinary citral yields two isomeric semicarbazones, one of which is formed in large amount and melts at 164°, whereas the second is produced in small amount only and melts at 171°. When the sodium hydrogen sulphite compound of citral is decomposed by sodium carbonate and shaken two or three times with ether, a portion of the citral is converted into the hydrosulphonic acid derivatives, whilst the remainder, amounting to about one-half of the total amount present, is dissolved by the ether; this fraction of the citral only yields the semicarbazone melting at 164°, and is therefore termed *citral a*. It boils at 118—119° under a pressure of 20 mm., has a sp. gr. = 0·8898, and an index of refraction 1·4891. In its chemical properties, it behaves in precisely the same way as ordinary citral; thus it can readily be converted into pseudo-ionone, which on inversion yields the ordinary ionone containing both the α- and β-modifications. The citral obtained by the decomposition of the hydrosulphonic acid derivatives referred to above yields a small amount of semicarbazone melting at 171°, and when repeatedly treated in a similar manner, it yields a much larger proportion of this semicarbazone, amounting finally to about 70 per cent. of the whole; it has not been found possible, however, to obtain a specimen which yields this semicarbazone exclusively. The fraction containing 70 per cent. of *citral b* does not differ in physical pro-

perties from citral *a*, and, like this, can be converted into ordinary pseudoionone. Citral *b* yields the ordinary citralidenecyanacetic acid melting at 122°, but this is accompanied by a substance melting at 80°, probably an isomeride. These results are in favour of the view that ordinary citral contains two geometrical isomerides; it is, however, not impossible that the formation of the semicarbazone melting at 171° may be due to the presence of some hitherto unsuspected impurity, which accumulates in the fraction known as citral *b*.

A. H.

Methods of Synthesis derived from the Study of Cyanals (Cyanhydrins of Aldehydes). By ALBERT COLSON (*Ann. Chim. Phys.*, 1897, [vii], 12, 231—257).—This paper refers to results already published (compare Abstr., 1895, i, 257; 1896, i, 282, 283, 346).

G. T. M.

Oxidation of Ketones. By E. VON COCHENHAUSEN (*J. pr. Chem.*, 1898, [ii], 58, 451—457).—In applying Benedikt and Zsigmondy's process (Benedikt-Ulzer, *Analyse der Fette*, 3rd Edt., 184), as modified by Herbig, for the detection of glycerol in purified wool fats, the author always found small amounts of oxalic acid; this was also the case with a specimen of pure wool fat, which had been prepared using acetone as the solvent. As the fat was free from glycerides, it was thought probable that the oxalic acid resulted from the oxidation of acetone, it being particularly difficult to free the fat from the last traces of this substance.

From a study of the action of potassium permanganate on pure acetone, the author finds that in alkaline solution, without heating, and when an insufficiency of the oxidising agent is employed, oxalic acid is the main product; with excess of permanganate, oxalic acid and carbonic anhydride are produced, whilst with very small amounts acetic acid is formed in addition to these two substances. It follows, therefore, that Popoff's law of the oxidation of ketones does not always hold good, and that Benedikt and Zsigmondy's test for the presence of glycerides in fatty mixtures is only of use in absence of acetone.

Experiments are now being made to see whether homologous ketones behave in a similar manner on oxidation. A. W. C.

Aliphatic Nitro-compounds with Multiple Functions. By LOUIS HENRY (*Chem. Centr.*, 1898, ii, 887, and *Rec. Trav. Chim.*, 17, 399—404; from *Bull. Acad. roy. Belg.*, [iii], 36, 149—154).—In continuation of his studies of the dependence of volatility and other properties on constitution, the author and his pupils have prepared compounds which contain the group $\cdot C \cdot NO_2$ and the group $:CO$ or $\cdot CN$ in the same molecule. *Nitracetone*, $CH_3 \cdot CO \cdot CH_2 \cdot NO_2$, prepared by the action of potassium dichromate and sulphuric acid on nitroisopropylic alcohol, is a limpid, colourless liquid with a pungent odour and burning taste; it is very slightly soluble in water, dissolves in alcohol and ether, boils at 152° under 717 mm. pressure, has a sp. gr. = 1·070 at 14°, and liberates carbonic anhydride from carbonates. *Nitrobutyronitrile*, $CN \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NO_2$, obtained by the action of silver nitrite on iodobutyronitrile, is a

colourless liquid with a faint odour and rather sweet, pungent taste ; it is insoluble in water, easily soluble in alcohol, ether, chloroform, and alkalis, has a sp. gr. = 1·138 at 12°, boils at 160° under 35 mm. pressure, and boils and decomposes at 236° under 760 mm. pressure. By the action of concentrated hydrochloric acid on nitrobutyronitrile at 50°, nitro-butyric acid is formed, whilst at higher temperatures it yields succinic acid and hydroxylamine hydrochloride. The author points out the influence of the various groups on the properties, and especially on the boiling points of the various compounds.   E. W. W.

Action of Nitrous Acid on Aliphatic Ketones. By GIACOMO PONZIO and AUSONIO DE-GASPARI (*J. pr. Chem.*, 1898, [ii], **58**, 392—402 ; also *Gazzetta*, 1898, **28**, ii, 269—279. Com-pare following abstract).—By the action of nitrous acid on ketones of the structure $CH_2Me \cdot CO \cdot CH_2 \cdot R$ (up to 9 carbon atoms), two isonitroso-ketones are formed, if the ketones have a normal structure, whereas if they have a tertiary structure only one isonitroso-ketone is produced. In the latter case, it is always the hydrogen of the methyl-ene group of the normal alcohol radicle which is displaced by the group NOH.

The structure of the isonitroso-ketones formed was proved by con-verting them into acyldinitro-hydrocarbons (according to a method already described), and subsequently hydrolysing them, when from a mixture of two isomeric isonitroso-ketones two fatty acids and two dinitro-hydrocarbons are obtained, whereas one isonitroso-ketone gives one fatty acid and one dinitrohydrocarbon.

Ethyl propyl ketone yields two isomeric isonitroso-ketones when treated with amylic nitrite and hydrochloric acid, from which dinitro-ethane and dinitropropane were obtained and separated by means of their potassium derivatives ; also, by conversion of the mixture into dioximes by Auwer's method, two substances were obtained and characterised by means of their osazones as acetylbutyrylosazone and dipropionylosazone.

Ethyl butyl ketone, prepared by the action of zinc ethyl on valeric chloride, is a pleasant smelling liquid boiling at 147—148° under a pressure of 742·9 mm. When treated with amylic nitrite, it yields two isonitroso-ketones, which were characterised by conversion into dinitroethane and dinitrobutane respectively.

Ethyl amyl ketone, prepared from zinc ethyl and normal hexoic chloride, gives two isomeric isonitroso-ketones, yielding dinitroethane and dinitropentane respectively.

Ethyl iso-amyl ketone, obtained by the action of zinc ethyl on iso-butyric chloride (b. p. 143—145° under 741·53 mm.), is a pleasant smelling liquid boiling at 163—163·5° under a pressure of 734·2 mm. Amylic nitrite converts it only into *isonitrosoethyl isoamyl ketone*, $C_5H_{11} \cdot CO \cdot CMe:NOH$, a pale, yellow oil. By the action of hydroxyl-amine, it is converted into acetylisohexyldioxime melting at 177—178°.

βa-Acetylisohexylphenylhydrazoxime, $C_5H_{11} \cdot C(N_2HPh) \cdot CMe:NOH$, prepared from the isonitroso-ketone and phenylhydrazine, crystallises from dilute alcohol in colourless leaflets melting at 113—114°.

β-Acetylisohexylphenylhydrazone, obtained from the phenylhydraz-

oxime by boiling with alcohol and hydrochloric acid, crystallises from alcohol in small, almost colourless needles melting at 92—93°. When heated at 150° with phenylhydrazine, it is converted into acetyliso-hexylosazone melting at 92—93°.

Ethyl isohexyl ketone, obtained by the action of zinc ethyl on isoheptoic chloride (isoamylacetic chloride, b. p. 168—169° under 739·44 mm.), is a fruity smelling liquid boiling at 185° under a pressure of 740·32 mm. Amylic nitrite converts it into *isonitrosoethyl isohexyl ketone*, a pale yellow oil.

Acetylisoheptyldioxime (acetylisoamylacetyldioxime),

$$C_6H_{13}\cdot C(NOH)\cdot CMe\colon NOH,$$
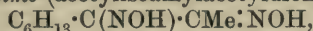
crystallises from alcohol in white needles melting at 169—170°.

βα-Acetylisoheptylphenylhydrazoxime crystallises from alcohol in pale yellow leaflets melting at 115—116°, and *acetylisoheptylosazone* forms yellow prisms melting at 133—134°.   A. W. C.

Acetylcaproyl [Methyl Amyl Diketone]. By GIACOMO PONZIO and O. PRANDI (*J. pr. Chem.*, 1898, [ii], **58**, 401—402; also *Gazzetta*, 1898, **28**, ii, 279—283. Compare preceding abstract).— *Acetylhexoyl* (2 : 3-octadione), $C_5H_{11}\cdot CO\cdot COMe$, prepared from its monoxime, isonitrosomethyl hexyl ketone, by the action of dilute sulphuric acid, is a yellow liquid boiling at 172—173° under a pressure of 732·8 mm.

αβ-Acetylhexoylphenylhydrazoxime, $C_5H_{11}\cdot C(NOH)\cdot CMe\colon N_2HPh$, crystallises from dilute alcohol in yellow needles melting at 110°.

α-Acetylhexoylphenylhydrazone forms glistening, yellow leaflets melting at 103—104° and *acetylhexoylosazone* yellowish-brown prisms melting at 117—118°.   A. W. C.

Isomorphous Formates of Calcium, Strontium, Barium, and Lead. By A. PLATHAN (*Chem. Centr.*, 1898, ii, 1009; from *Diss. Helsingfors*, 1897, 46).—The formates of calcium, strontium, barium, and lead were prepared in crystals by evaporating their solutions at 10° and 73°, and by slowly cooling solutions saturated at 100°. These salts are isomorphous and crystallise in rhombic, sphenoidal forms, and not in holohedral forms, as hitherto supposed; the densities and equivalent volumes were determined and the topic axes (Muthmann) and crystal volumes (Schrauf) were calculated. The equivalent volumes of the formates, like those of the sulphates and carbonates, increase from the calcium through the strontium and lead salts to the barium, that of the lead salt being nearly equal to that of the strontium salt. The topic ψ-axis shows a similar variation, but lead formate has the largest refractive index and molecular refraction. The solubility of the salts at 25° was determined; a complete series of crystalline mixtures of the lead and barium salts were prepared at 25°, and from analyses of the salts and the mother liquors, a curve was plotted, showing the relationship of the composition of the crystals and the solution. Strontium formate crystallises with $2H_2O$ at the ordinary temperature, but if the solution is evaporated at above 71·9°, the anhydrous salt separates. By allowing mixed solutions of the strontium and lead salts to crystallise at 25°, it was found that when 79 per cent. or less of the former salt was present, a mixture of

anhydrous salts crystallises, whilst from solutions containing a larger proportion of this salt a mixture of formates containing $2H_2O$ was obtained. [.... ....]   **E. W. W.**

Fluorodibromacetic Acid. By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1898, ii, 702—704 ; from *Bull. Acad. roy. Belg.*, [iii], **35**, 849—868. Compare Abstr., 1898, i, 457).—Fluorodibromacetic fluoride may be prepared by heating a mixture of tribromacetic chloride (3 mols. : obtained by the action of phosphorus pentachloride on tribromacetic acid), antimony fluoride (2 mols.), and bromine ($\frac{1}{3}$ mol.) in a platinum vessel. The action takes place slowly, for in one case after 14 days only $\frac{4}{5}$ths of the antimony fluoride was found to have been attacked. After removing the excess of bromine by cautiously adding powdered antimony and distilling off the antimony bromide, the product, when fractionated, yields fluorochlorobromacetic fluoride, which distils at 51° and fluorodibromacetic fluoride ; the former is probably formed by the action of the antimony chloride, which may result from the action of the fluoride on tribromacetic chloride, on a portion of the fluorodibromacetic fluoride. The latter is a colourless liquid with a pungent odour, boils at 74·5°, acts violently on alcohol and water, but only attacks glass at a high temperature. Its vapour density was determined. From 200 grams of tribromacetic chloride only about 30 grams of fluorodibromacetic fluoride is obtained, tribromacetic chloride, tribromacetic fluoride, derivatives of fluorochlorobromacetic acid, and probably of dibromacetic acid being also formed. Fluorodibromacetic acid is also obtained as a bye-product in the preparation of fluorochlorobromacetic acid. Fluorodibromacetic acid is prepared by adding ice to fluorodibromacetic fluoride cooled to − 25°, removing the water and hydrogen fluoride by keeping the product in a vacuum over alkali, and finally distilling under a pressure of 50—60 mm. It is a strong acid, forms colourless crystals, is very hygroscopic, melts at 26·5°, boils at 130° under 60 mm. and at 198° under 760 mm. pressure, is easily soluble in water and alcohol, and soluble in ether and chloroform. When an aqueous solution of the acid or its salts is boiled, fluorodibromomethane is formed. All the salts are easily soluble in water and alcohol, and when heated leave a residue of bromide ; the sodium salt crystallises best from a mixture of alcohol and ether ; the potassium salt crystallises from alcohol in leaflets and is not hygroscopic, and the barium salt contains $6H_2O$. Ethylic fluorodibromacetate is a colourless liquid with a pleasant odour like that of camphor, boils at 173°, has a sp. gr. $= 1·7851$ at 12° and $= 1·77097$ at 30°; its vapour density was determined. *Fluorodibromacetamide,* prepared by shaking ethylic fluorodibromacetate with a saturated solution of ammonia, crystallises from water in prisms, melts at 136°, sublimes at 100°, and is slightly soluble in water, being more soluble than fluorodichloracetamide. The conductivity and amount of dissociation of solutions of fluorodibromacetic acid and tribromacetic acid and the conductivity of solutions of their sodium salts were determined. Of the substituted acetic acids, those containing fluorine are the strongest acids, and fluorodibromacetic acid is a stronger acid than either fluorochlorobromacetic or fluorodichloracetic acid. The substitution

of bromine for chlorine has apparently no influence on the strength
of the acid.   E. W. W.

**Alkylic Salts of the Monochloro-derivatives of Normal
Butyric Acid and the Volatility of Chlorine and Oxygen
Compounds.** By Louis Henry (*Chem. Centr.*, 1898, ii, 273; from
Bull. Acad. roy. Belg., [iii], **35**, 507—520).—The author has prepared
the methylic, allylic, and propylic salts of α-, β-, and γ-chlorobutyric
acids by the action of the corresponding alcohols on the α-, β-, and
γ-chlorobutyronitriles (see this vol., i, 183) respectively; the vapour
densities of the compounds and their physical constants were
determined. The boiling points of these derivatives show that the
greater the proximity of the chlorine and oxygen atoms in the
molecule, the lower the boiling point; in the γ-derivatives this
influence is no longer apparent. The β-chloro-derivatives can also be
prepared by the action of hydrochloric acid on the corresponding
alkylic salts of crotonic acid or by the direct chlorination of the
butyrates.   E. W. W.

**Solidifying Points of Mixtures of Stearic and Palmitic
Acids.** By L. E. O. de Visser (*Rec. Trav. Chim.*, 1898, **17**,
346—348. Compare Abstr., 1898, i, 560).—When 100 grams of
a mixture of palmitic and stearic acids, containing 47·5 per cent.
of the latter, is agitated in the form of thin shreds with 600 c.c. of
absolute alcohol during 2 minutes, the solidifying point (56·4°) of the
portion remaining undissolved does not differ from that of the
original mixture; the latter, therefore, must be considered as a
solid solution existing in only one form of crystalline aggregation.
The eutectic mixture of the two acids, which solidifies at 54·82° and
contains 29·76 per cent. of stearic acid (*loc. cit.*), is shown, however,
to be a mixture of two solid modifications by its melting at 55·09°
after being agitated with absolute alcohol; this melting point corre-
sponds with that of a mixture containing 31·78 per cent. of stearic acid,
so that the modification more easily soluble in alcohol must contain a
greater amount of stearic acid than that originally present in the
eutectic mixture.   W. A. D.

Constitution of the Crotonic Acids. By Fritz Fichter and
A. Krafft (*Chem. Centr.*, 1898, ii, 1011, from *Arch. Sci. phys. nat.
Genève*, [iv], **6**, 402—403).—Since β-hydroxyglutaric acid, when dis-
tilled in a vacuum, yields, not only glutaconic acid, but also isocrotonic
acid, the latter must have a constitution corresponding with vinylacetic
acid, $CH_2:CH\cdot CH_2\cdot COOH$, and hence the crotonic acids are not
stereoisomerides, but differ constitutionally in the position of the
double bond.   E. W. W.

Derivatives of Aliphatic Hydroxynitriles. By Louis Henry
(*Chem. Centr.*, 1898, ii, 661—662; from *Bull. Acad. roy. Belg.*, [iii],
36, 22—30. Compare this vol., i, 182).

I. Hydroxynitriles containing C_4.

α-*Methyllactonitrile*, $CN\cdot CHMe\cdot CH_2\cdot OH$, is prepared by the action of
potassium cyanide on the monochlorhydrin, $CHMeCl\cdot CH_2\cdot OH$, or by
the addition of hypochlorous acid to propylene; it boils at 230—235°.

Dimethylglycollonitrile or *dimethylacetonecyanhydrin*, $OH \cdot CMe_2 \cdot CN$, is obtained by the combination of hydrogen cyanide with dimethyl ketone; by the action of acetic chloride, it yields the *acetate*, $OAc \cdot CMe_2 \cdot CN$, a colourless liquid, which boils at 180—182°, has a sp. gr. = 0·997 at 19°, and with phosphoric anhydride yields the *nitrile* of *α-methylacrylic acid* (see following abstract). By the action of phosphorus pentachloride on dimethylglycollonitrile, *chloracetonitrile*, $CMe_2Cl \cdot CN$, and the nitrile of α-methylacrylic acid are obtained.

II. HYDROXYNITRILES CONTAINING C_5.

Isobutylidenecyanhydrin, $CHMe_2 \cdot CH(OH) \cdot CN$, prepared by the action of hydrogen cyanide on isobutaldehyde, with phosphorus pentachloride, yields *α-chlorisopropylacetonitrile*, $CHMe_2 \cdot CHCl \cdot CN$, which is a limpid, colourless liquid, has an odour like that of amylic compounds, boils at 154° under 750 mm. pressure, has a sp. gr. = 0·9922 at 10°, and when distilled with phosphoric anhydride, yields the *nitrile* of *β-dimethylacrylic acid* (see following abstract). A comparison of the isobutyl with the normal butyl derivatives shows that the introduction of a chlorine atom into the group $CH_2 \cdot CN$, raises the boiling point about 24°, whilst the introduction of another methyl group into the group CH_2Me raises the boiling point about 12°. *Cyanobutyryl acetate*, $CHMe_2 \cdot CH(OAc) \cdot CN$, is a colourless liquid with an unpleasant, bitter taste, boils at 192—193°, and has a sp. gr. = 0·9745 at 19°.

III. HYDROXYNITRILES CONTAINING C_6.

By the action of phosphorus pentachloride, isovalerylcyanhydrin *monochlorisobutylacetonitrile* or *α-chlorocapronitrile*, is converted into $CHMe_2 \cdot CH_2 \cdot CHCl \cdot CN$; this is a colourless liquid of pleasant odour and pungent taste, boils at 172—173° under 755 mm. pressure, has a sp. gr. = 0·984 at 12°, is insoluble in water, and by the action of acetic chloride yields *cyanisovaleryl acetate*, $CHMe_2 \cdot CH_2 \cdot CH(OAc) \cdot CN$, a colourless, limpid liquid which boils at 204° and has a sp. gr. = 0·960 at 19°. By the action of phosphoric anhydride on amylidene cyanhydrin, the unsaturated nitrile, $CHMe_2 \cdot CH:CH \cdot CN$ (see following abstract) is obtained.

IV. HYDROXYNITRILES CONTAINING C_8.

By the action of phosphorus pentachloride on *œnanthylidenecyanhydrin*, $CH_3 \cdot [CH_2]_5 \cdot CH \cdot (OH) \cdot CN$, prepared by the addition of hydrogen cyanide to œnanthaldehyde. *α-chlorocapronitrile*,
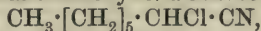
$$CH_3 \cdot [CH_2]_5 \cdot CHCl \cdot CN,$$

is obtained as a colourless liquid with an odour like œnanthaldehyde; it boils at 124° under 38 mm., and at 217° under 755 mm. pressure, and has a sp. gr. = 0·959 at 12°. *α-Acetylœnanthylidenecyanhydrin*, $CH_3 \cdot [CH_2]_5 \cdot CH(OAc) \cdot CN$, is a colourless liquid, with a bitter taste, boils at 245°, and has a sp. gr. = 0·9385 at 19°.   E. W. W.

Unsaturated Compounds. By LOUIS HENRY (*Chem. Centr.*, 1898, ii, 662—663; from *Bull. Acad. roy. Belg.*, [iii], **36**, 31—54).

I. UNSATURATED NITRILES.

By the action of phosphoric anhydride on hydroxynitriles, unsaturated nitriles are often formed, but lactonitrile, $CN \cdot CHMe \cdot OH$, does not yield acrylonitrile.

Unsaturated Nitriles containing C_4.—The hydroxynitriles containing C_4, with one exception, when heated with phosphoric anhydride, lose $1H_2O$. Acetonecyanhydrin or dimethylglycollonitrile gives a good yield of *a-methylacrylonitrile*, CH_2:$CMe\cdot CN$, which is a colourless, limpid liquid with a strong odour and a bitter taste, boils at 90—92°, has a sp. gr. = 0·7991 at 18°, and is insoluble in water. By comparing the corresponding nitriles, it is seen that the saturated nitriles containing C_3 boil about 20°, and the saturated nitriles containing C_4 about 18° higher than the unsaturated nitriles. By the action of phosphoric anhydride on *a*- or *β*-hydroxybutyronitrile, *β-methylacrylo-nitrile*, $CHMe$:$CH\cdot CN$, is formed; this boils at 118—119°; γ-hydroxy-butyronitrile is completely charred by the action of phosphoric anhy-dride. *Vinylacetonitrile*, $CN\cdot CH_2\cdot CH$:CH_2, prepared by distilling the chloride, $CN\cdot CH_2\cdot CH_2\cdot CH_2Cl$, with dry potassium hydroxide, is a colourless liquid with a pleasant odour and pungent taste; it boils at 135° and has a sp. gr. = 0·911 at 16°.

Unsaturated Nitriles containing C_5.—By the action of phosphoric anhydride on isobutylidene cyanhydrin, *β-dimethylacrylonitrile*, $CN\cdot CH$:CMe_2, is obtained; it is a colourless liquid with a pleasant odour and a pungent taste, boils at 140—142°, has a sp. gr. = 0·8292 at 14°, is insoluble in water and soluble in alcohol and ether.

Unsaturated Nitriles containing C_6.—γ-Dimethylcrotononitrile or *β-isopropylacrylonitrile*, $CHMe_2\cdot CH$:$CH\cdot CN$, prepared by the action of phosphoric anhydride on amylidene cyanhydrin,

$$CHMe_2\cdot CH_2\cdot CH(OH)\cdot CN,$$
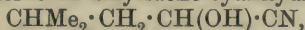
is a colourless liquid with a pleasant odour, boils at 154—155° under 754 mm. pressure, has a sp. gr. = 0·8268 at 16°, is insoluble in water, and soluble in alcohol, ether, &c.

Unsaturated Nitriles containing C_8.—By the action of phosphoric anhydride on œnanthylidene cyanhydrin, *γ-butylcrotononitrile*, $CH_3\cdot[CH_2]_4\cdot CH$:$CH\cdot CN$, is formed; it is a colourless liquid with an unpleasant taste, boils at 197—200°, has a sp. gr. = 0·8318 at 16°, is insoluble in water, but soluble in alcohol and ether. The unsaturated nitriles containing C_4, C_6, and C_8 have the same boiling points as the corresponding saturated nitriles.

In the original paper, tables showing the influence of the substitution of a methyl group for a hydrogen atom, on the boiling points of unsaturated nitriles, and tables showing the boiling points of the corresponding saturated and unsaturated nitriles, are given for each series.

II. DERIVATIVES OF CROTONIC ACID.

Crotonic chloride, $CHMe$:$CH\cdot COCl$, prepared by the action of phos-phorus pentachloride on crotonic acid, is a colourless, fuming liquid with an oppressive odour, boils at 124—125°, and has a sp. gr. = 1·295 at 16°.

Ethylic β-chlorobutyrate, $CHMeCl\cdot CH_2\cdot COOEt$, is obtained by the action of alcohol on crotonic chloride, or by adding hydrochloric acid to ethylic crotonate; it boils at 165—170°.

III. *A*. DERIVATIVES OF ALLYLACETIC ACID. [With CAMILLE ASCHMANN, *Diss. Löwen*, 1883].

Allylacetic acid is prepared by boiling ethylic allylacetate with the calculated quantity of a solution of 140 parts of potassium hydroxide

in 40 parts of water; the *chloride*, $CH_2:CH \cdot CH_2 \cdot COCl$, obtained by the action of phosphorus trichloride on the acid, is a thin, colourless, fuming liquid with an oppressive odour, boils at 128° under 765 mm. pressure and has a sp. gr. = 1·0739 at 16°. *Allylacetamide*,

$$C_3H_5 \cdot CH_2 \cdot CO \cdot NH_2,$$
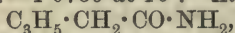
crystallises in white leaflets, melts at 94°, boils at 230° under 770 mm. pressure and is soluble in water, alcohol, and ether. *Allylacetonitrile*, $C_3H_5 \cdot CH_2 \cdot CN$, has a pleasant odour, boils at 140°, has a sp. gr. = 1·1803 at 13°, and is insoluble in water. The allylacetyl derivatives have the same boiling points as the corresponding valeryl derivatives. *Chlorhydroxyvaleric acid*, $OH \cdot CH_2 \cdot CHCl \cdot CH_2 \cdot CH_2 \cdot COOH$, prepared by the union of hypochlorous acid with allylacetic acid, is a colourless liquid, heavier than water, decomposes on heating, and is slightly soluble in water. Ethylic allylacetate combines with iodine monochloride in aqueous solution, forming crystals which melt at 61°.

B. Allylacetone, $C_3H_5 \cdot CH_2 \cdot COMe$.—This can be prepared by boiling ethylic allylacetate with aqueous potassium carbonate solution; it combines easily with hypochlorous acid to form the *chlorhydrin*, $OH \cdot C_3H_5Cl \cdot CH_2 \cdot COMe$, a colourless, viscous liquid, which cannot be distilled under the ordinary pressure, and is heavier than water.

C. Fumaric acid.—By the action of hypochlorous acid on ethylic fumarate, *ethylic dichlorosuccinate*, $C_2H_2Cl_2(COOEt)_2$, is formed; it crystallises in colourless needles and melts at 57°. Since hypochlorous acid does not combine with ethylic fumarate, whilst it easily unites with ethylene, the displacement of a hydrogen atom by the COOEt group apparently lessens the additive power of an unsaturated compound. Perchlorethylene does not combine with hypochlorous acid.

<div align="right">E. W. W.</div>

Methylic γ-Cyanodimethylacetoacetate. By MAX CONRAD and RICHARD GAST (*Ber.*, 1899, **32**, 137—145. Compare Lawrence, Proc., 1898, 251).—The cyanogen radicle in this compound can be displaced in the same manner as the bromine in methylic γ-bromodimethylacetoacetate; thus, with aqueous thiourea, it forms hydrocyanic acid and methylic amidothiazylisobutyrate, whilst with piperidine it gives methylic γ-piperidyldimethylacetoacetate; with aniline, it gives methylic γ-anilidodimethylacetoacetate, which loses methylic alcohol and is converted into phenyldimethylketopyrrolidone, $NPh {\displaystyle <} {CH_2 \cdot CO \atop CO—CMe_2}$.

On hydrolysis with hydrochloric acid or with baryta, an acid, $C_7H_{10}O_5$, is obtained. This melts at 214°, and the authors show that it is the *monolactone* of *βγ-dihydroxy-aa-dimethylglutaric acid*,

$$CMe_2 {\displaystyle <} {CH(OH) \atop CO—-O} {\displaystyle >} CH \cdot COOH,$$

and not β-hydroxy-aa-dimethylglutaconic acid,

$$COOH \cdot CMe_2 \cdot C(OH):CH \cdot COOH,$$
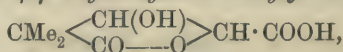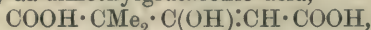
as was supposed by Lawrence. The *barium* salt, *calcium* salt, $Ca(C_7H_9O_5)_2, 4H_2O$, and *silver* salt, $AgC_7H_9O_5$, were prepared. The lactone can be hydrolysed by boiling with baryta water, when the *barium* salt of *βγ-dihydroxy-aa-dimethylglutaric acid* is produced; the

corresponding acid could not be isolated. The acid, $C_7H_{10}O_4$, prepared
by the action of hydriodic acid on the acid $C_7H_{10}O_5$, is regarded by
the authors as the *lactone* of *αα-dimethyl-γ-hydroxyglutaric acid*,

$$\begin{array}{c} CMe_2 \cdot CH_2 \\ CO \underline{} O \end{array}\!\!\!> CH \cdot COOH,$$ whilst Lawrence regarded it as αα-dimethyl-

glutaconic acid, $COOH \cdot CH \colon CH \cdot CMe_2 \cdot COOH$.   T. M. L.

Products of Oxidation of Hydroxygluconic Acid. By Léon
Boutroux (*Compt. rend.*, 1898, **127**, 1224—1227).—The author has
isolated a hydroxygluconic acid as a product of oxidation of gluconic
acid by a bacterium in presence of calcium carbonate. The acid, which
closely resembles a hydroxygluconic acid recently obtained by
Bertrand (*Proès-verbal Soc. Chim.*, Nov. 11, 1898), may be oxidised
with dilute nitric acid, affording racemic acid, a trihydroxyglutaric
acid, glyoxylic acid, and αβ-dihydroxybutyric acid. The formation of
these substances is held to justify the formula

$$\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{OH \cdot CH_2 \cdot CO \cdot C}} \underline{} \underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}} \underline{} \underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}} \underline{} COOH,$$
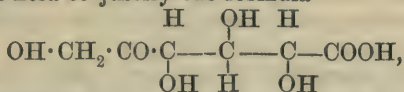
as representing the structure of the hydroxygluconic acid in question.
                                                                        A. L.

Action of Ethylic Malonate on Unsaturated Ketones. By
Daniel Vorländer and S. Gärtner (*Annalen*, 1898, **304**, 1—24.
Compare Abstr., 1897, i, 272).—Phorone behaves differently towards
ethylic sodiomalonate according as the latter is dissolved in absolute
alcohol or is suspended in ether.

Phoronediacetic acid, $CO(CH_2 \cdot CMe_2 \cdot CH_2 \cdot COOH)_2$, is prepared by
adding phorone to ethylic sodiomalonate (2 mols.), suspended in
ether or benzene, and heating the mixture during 24 hours at the
boiling point of ether; it crystallises from boiling water in lustrous
leaflets, or long, flattened needles, and melts at 110°. The *barium*
salt forms prisms containing $3H_2O$, and the *silver* salt resists the
action of light; the *methylic* salt boils at 183—184° under a pressure
of 25 mm. The *oxime* crystallises from water in aggregates of prisms,
and melts at 141—143°; the *anhydride* melts at 49°. The acid is
but slowly attacked by a cold solution of potassium permanganate, but
at 70—100°, in presence of sodium carbonate, it becomes oxidised to
unsymmetrical dimethylsuccinic acid; the latter is also produced
when dimethylhydroresorcinol is oxidised with potassium perman-
ganate.

The *anhydride*, $C_9H_{12}O_4$, is a bye-product in the preparation of
phoronediacetic acid, and is also produced during the formation of
dimethylhydroresorcinol from mesitylic oxide and ethylic malonate;
it crystallises in prisms, or needles, and melts at 135°.

γ-Acetyl-ββ-dimethylbutyric acid, $COMe \cdot CH_2 \cdot CMe_2 \cdot CH_2 \cdot COOH$, is
another product of the action of phorone on ethylic sodiomalonate;
the *methylic* salt boils at 215°, and the *semicarbazone* crystallises from
boiling water in prisms, and melts at 172°, when it decomposes.

The *anhydride*, $C_{13}H_{18}O_4$, results from the action of ethylic sodio-

malonate on pulegone in molecular proportion ; it crystallises from dilute alcohol in prisms, and melts at 104°.

Methylcyclohexenone is indifferent towards ethylic sodiomalonate.

M. O. F.

Triethylic Isaconitate (ω_2-Δ-ω_1-Propenetricarboxylate). By MAX GUTHZEIT and LEOPOLD LASKA (*J. pr. Chem.*, 1898, [ii], 58, 403—441).—Ethylic isaconitate (ethylic ω_2-Δ-ω_1-propenetricarboxylate), $C_{12}H_{18}O_6$, prepared from ethylic ethoxylcoumalindicarboxylate by the method already given (Abstr., 1889, 860), boils at 176—178° under a pressure of 17 mm. The dry *sodium* derivative is a reddish-yellow powder, soluble in water, forming a yellow solution, which gives precipitates with copper, silver, cadmium, lead, cobalt, nickel, zinc, and barium salts.

Ethylic ethylisaconitate, $CEt(COOEt)_2 \cdot CH:CH \cdot COOEt$, obtained by the action of sodium and ethylic iodide on ethylic isaconitate in alcoholic solution, is an oil boiling at 176—177° under a pressure of 18 mm. The corresponding *benzyl* derivative is a colourless oil boiling at 237—239° under a pressure of 23 mm.

When ethylic isaconitate is hydrolysed with hydrochloric acid, 50 per cent. of the theoretical amount of glutaconic acid is obtained, together with hydroxyglutaric acid and butyrolactonecarboxylic acid ; potassium hydroxide in the cold produces the same effect, the absence of malonic acid in both cases showing that the chain has not been broken. With barium hydroxide, the chain is broken, for besides glutaconic and hydroxyglutaric acids, malonic, acetic, and formic acids are also produced.

When heated with aniline at 150°, ethylic isaconitate is decomposed into malonamide, and a substance which could not be obtained pure, but which is possibly the anilide of β-anilidoacrylic acid ; paratoluidine reacts in an analogous manner.

Triethylic β-anilido-α-carboxylglutarate,

$$COOEt \cdot CH_2 \cdot CH(NHPh) \cdot CH(COOEt)_2,$$
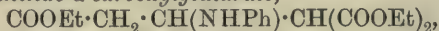
is obtained as a yellow oil by the action of aniline on ethylic isaconitate in the cold ; ferric chloride gives a black coloration with it. The *hydrochloride*, $C_{16}H_{25}NO_6,HCl$, separates from absolute ether in needle-shaped crystals which melt at 160°, resolidify at once, and melt for the second time at 176—177° ; this is probably due to the elimination of alcohol with formation of an oxyquinoline derivative. It is decomposed by water, and yields ethylic malonate when heated to 150°.

Ethylamine acts on ethylic isaconitate in a similar manner to aniline, even when very dilute, with formation of malonodiethylamide ; ammonia never produces a fission of the carbon chain, but leads to the formation of ring compounds, which can be readily explained on the assumption that the ethereal salt exists in the enolic form.

The *ammonium* derivative of *ethylic 2-hydroxy-$\Delta_{2,4}$-hydropyridone-3-carboxylate*, $\begin{array}{l} CO \cdot NH \cdot C \cdot O \cdot NH_4 \\ CH:CH \cdot C \cdot COOH \end{array}$, obtained by the action of a saturated aqueous solution of ammonia on ethylic isaconitate at 0°, is a light yellow powder which becomes red when heated to 200°, and

melts about 215°. When boiled with alkalis, ammonia is eliminated, and when dissolved in concentrated hydrochloric acid, and then treated with water, it gives rise to *ethylic 2-hydroxy-$\Delta_{2,4}$-hydropyridone-3-carboxylate*, $CO\underset{CH=\!\!=\!\!CH}{\overset{NH\cdot C(OH)}{<\qquad\qquad>}}C\cdot COOEt$, which crystallises from acetone in glistening, silken needles, melts at 183°, gives a blood-red coloration with ferric chloride in alcoholic solution, but does not give a precipitate with picric acid. The ammonium salt gives precipitates with silver, copper, lead, zinc, barium, and magnesium salts. When fused with phthalic anhydride, the melt dissolves in water with a red coloration, and gives a beautiful blue fluorescence with ammonia, a reaction which Ruhemann (Trans., 1893, 259) has shown to be characteristic for metadihydroxypyridine. The basic properties of this substance are very slight. The *silver* salt prepared from the sodium derivative by the action of silver nitrate is a white substance not readily decomposed by light. The *ethyl* derivative,

$$CO\underset{CH=\!\!=\!\!CH}{\overset{NH\cdot C(OEt)}{<\qquad\qquad>}}C\cdot COOEt,$$
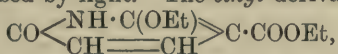
obtained from the silver salt by interaction with ethylic iodide, separates from light petroleum in white crystals melting at 66—67°. Ferric chloride colours the alcoholic solution yellowish-red.

2-Hydroxy-$\Delta_{2,4}$-hydropyridine-3-carboxylic acid, prepared from the ethylic salt by the action of concentrated sulphuric acid, crystallises in needles, melts in a closed tube at 197—198°, gives no blue coloration with potassium nitrite, and its ammoniacal solution gives precipitates with silver, copper, lead, and barium salts. It is isomeric, not identical with Ost's comenamic acid (Abstr., 1883, 792). Bromine oxidises the acid, but with the ethylic salt, gives a *substitution product*, $C_8H_8O_4NBr$, which is coloured bluish-black, without melting, when heated to 210°.

When the ethylic salt is heated at 250—260° with phosphorus pentachloride and phosphorus oxychloride in sealed tubes, it is converted into *aa'-dichloronicotinic acid*, $CCl\underset{CH\!:\!CH}{\overset{N\!-\!CCl}{<\qquad\quad>}}C\cdot COOH$, which separates from ether in yellow crystals melting at 135—136°, but from a mixture of ether and light petroleum in white needles melting at 144°.

When the mother liquors from the hydrodioxypyridine derivative are evaporated, they yield a small amount of the *amide* of hydrodioxypyridinecarboxylic acid, $CO\underset{CH=\!\!=\!\!CH}{\overset{NH\cdot C(OH)}{<\qquad\qquad>}}C\cdot COOH$, melting with evolution of gas at 206°.

When hydrolysed with alcoholic potash or barium hydroxide, ethylic benzylisaconitate is converted into benzylglutaconic acid,

$$COOH\cdot CH(CH_2Ph)\cdot CH\!:\!CH\cdot COOH,$$
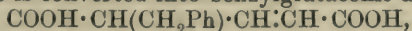
melting at 150—152°; neither aniline nor ammonia produces either an additive product or causes fission of the carbon chains, but substances, probably pyridine derivatives, which readily suffer oxidation are formed.

Ethylic carboxyglutarate (ethylic ω_2-ω_1-propanetricarboxylate), $COOEt\cdot CH(COOEt)\cdot CH_2\cdot CH_2\cdot COOEt$, obtained from ethylic isaconitate by the action of zinc dust and acetic acid, is a liquid boiling

at 171° under a pressure of 18 mm. Ferric chloride does not produce a blue colour, and when heated with alcoholic ammonia, *carboxyglutaramide*, $CONH_2 \cdot CH(CONH_2) \cdot CH_2 \cdot CH_2 \cdot CONH_2$, is produced crystallising in needles melting at 181°.   A. W. C.

A Double Citrate of Zirconium and Ammonium. By S. H. HARRIS (*Amer. Chem. J.*, 1898, **20**, 871—872).—On adding a 10 per cent. solution of ammonium citrate to an aqueous solution of the mixed chlorides obtained by dissolving zirconium hydroxide in concentrated hydrochloric acid, and repeatedly recrystallising the product, a white, curdy precipitate separates, which very easily dissolves in an excess of ammonium citrate; when dried at 120°, it has the composition $Zr_2C_6H_5O_7(NH_4)_3$, and is very deliquescent.   W. A. D.

Influence of Formation of Salts on the Hydrolysis of Amides and Ethereal Salts by Alkalis. By EMIL FISCHER (*Ber.*, 1898, **31**, 3266—3277).—Among the members of the uric acid group, compounds which contain hydrogen replaceable by metals are much less readily hydrolysed by alkalis than compounds in which the hydrogen has been replaced by methyl or some other group; thus, whilst uric acid itself can be boiled with an excess of normal alkali for a long time without undergoing much decomposition, tetramethyluric acid is rapidly decomposed even in the cold, the mono-, di-, and tri-methyluric acids standing in an intermediate position between these extremes. The ease with which the decomposition can be effected seems also to depend on the constitution of the compound, 1 : 3 : 9-trimethyluric acid, for example, being much more readily decomposed than the 1 : 7 : 9-derivative. Similar relations hold in the series of the xanthine and hypoxanthine derivatives, as well as among the chloro-purines and bromoxanthines. Thus xanthine is much more stable towards alkalis than theobromine, whilst the latter is again more stable than caffeine, and the same gradation exists between the bromine derivatives of these compounds; the same difference has been found to exist in many other series of compounds. Thus cyanuric acid is much more stable than trimethylic isocyanurate towards alkalis, the former being scarcely affected, whereas the latter is converted even at 40—45° into *trimethylbiuret*, $C_5H_{11}N_3O_2$, which crystallises in slender needles and melts at 126° (corr.) Again, salicylamide, $OH \cdot C_6H_4 \cdot CO \cdot NH_2$, is much less readily attacked than methylsalicyl-amide, $OMe \cdot C_6H_4 \cdot CO \cdot NH_2$, and, similarly, methylic salicylate is more resistant than methylic methylsalicylate, $OMe \cdot C_6H_4 \cdot COOMe$. Analogous results have been obtained with methylic parahydroxybenzoate and methylic anisate; ethylic acetoacetate and ethylic dimethylacetoacetate; hippuric acid, $NHBz \cdot CH_2 \cdot COOH$, and benzoylmethylamide, $NHMeBz$, and potassium cyanide and acetonitrile. A similar difference in behaviour is also exhibited by certain compounds towards potassium hydrosulphide; trichloropurine, for example, not being affected by this reagent, whilst 7-methyltrichloropurine is converted by it into thiochloropurine. No direct relation has been ascertained between this phenomenon and the heats of formation of the various substances concerned. It is to be noted that the compounds which offer the greatest resistance to alkalis are acid substances, and as such become electrolytically dis-

sociated in solution, and it seems possible that the complex negative ions thus formed may exert an electrical repulsion on the similarly charged hydroxyl ions which in some way hinders the chemical action.

A. H.

Mercurydimethyl. By EUGEN BAMBERGER (*Chem. Centr.*, 1898, ii, 1015; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 385—386).—By the action of nitric peroxide on mercurydimethyl, an extremely unstable acid, $C_2H_5N_3O_4$, which crystallises in white needles and melts at 65—70°, is obtained. On decomposition, it yields formic acid, carbonic anhydride, nitrous oxide, nitrogen, ammonia, and hydroxylamine, with some carbonic oxide and formaldehyde. According to the author, the acid is probably the *dioxime of imidocarbonic acid*, $NH[C(OH):N \cdot OH]_2$.

E. W. W.

1 : 1-Dimethyltrimethylene. By GABRIEL GUSTAVSON and (Miss) O. POPPER (*J. pr. Chem.*, 1898, [ii], 50, 458—461).—*Pentaglycol bromide*, $CMe_2(CH_2Br)_2$, obtained by the action of phosphorus tribromide on pentaglycol, boils at 185—190° at atmospheric pressure, and when treated with zinc dust in alcoholic solution, yields 1 : 1-*dimethyltrimethylene*, $\begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix} > CMe_2$, boiling at 21°. This has a slight odour resembling that of naphtha; a sp. gr. = 0·6604 at 20°/4°; and a refractive index = 1·3659; it is fairly stable towards potassium permanganate, but combines readily with bromine in the cold. That the substance has the above constitution, and is not isopropylethylene, is shown by the facts that it combines with hydriodic acid to form dimethylethylcarbinylic iodide, that its bromine compound, $C_5H_{10}Br_2$, when reduced, does not give the original hydrocarbon, but trimethylethylene, and that it dissolves in dilute sulphuric acid, whereas isopropylethylene does not.

The ease with which the hydrocarbon unites with bromine is not contradictory to the above formula, when it is remembered that the corresponding acid, $\begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix} > C(COOH)_2$, is readily acted on by bromine and hydrobromic acid.

A. W. C.

Chlorination of Benzene in Presence of Aluminium Chloride. By A. MOUNEYRAT and CH. POURET (*Compt. rend.*, 1898, 127, 1025—1027. Compare this vol., i, 1).—Aluminium chloride has been shown to be a powerful chlorinating agent in the aliphatic series (Abstr., 1898, i, 613), and the authors' experiments indicate that it plays the same part when applied to aromatic substances. One molecular proportion of chlorine is rapidly absorbed when passed into dry benzene mixed with 3 per cent. of aluminium chloride at 50—55°; the product mainly consists of chlorobenzene together with a mixture of the three dichlorobenzenes and unaltered hydrocarbon. When the monochloroderivative is chlorinated in a similar manner, paradichlorobenzene predominates in the product and is partially separated from its isomerides by cooling the mixture in ice; the mother liquor from the crystals of the para-compound yields, on fractionation, a further quantity of this substance and the meta-isomeride. The following chloro-derivatives are obtained when benzene or its mono- and di-chloro-

derivatives are further chlorinated in the presence of the same amount of aluminium chloride : the three trichlorobenzenes, a tetra-chlorobenzene melting at 134° and boiling at 240°, pentachlorobenzene, and hexachlorobenzene.   G. T. M.

Mixed Phenylic Ethylic Phosphates. By ALBERT MOREL (*Compt. rend.*, 1898, **127**, 1023—1025. Compare this vol., i, 29).—*Diphenylic ethylic phosphate*, $PO(OPh)_2 \cdot OEt$, prepared by the action of ethylic dichlorophosphate on dry sodium phenoxide at 0°, is a colourless, highly refractive oil with a fish-like odour boiling at 250—263° under a pressure of 70 mm. ; it decomposes when distilled under the ordinary pressure.

Phenylic diethylic phosphate, $PO(OEt)_2OPh$, produced by slowly adding diethylic chlorophosphate to dry sodium phenoxide cooled by ice, is an oil greatly resembling the preceding compound, but rather more volatile ; it boils at 210—230° under a pressure of 70 mm.

                                                        G. T. M.

Synthesis of Phenol from Acetylene. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, **127**, 908—911).—The author has made experiments with a view to define the conditions under which acetylene is converted into phenol, with intermediate formation of a sulphonic acid. Pure and dry acetylene is passed for about 18 hours through sulphuric acid containing about 30 per cent. of sulphuric anhydride. The liquid is then diluted and neutralised with potassium carbonate, and the potassium sulphate and a crystallisable sulphonate, $C_2H_4O_2(SO_3K)_2$, are separated, partly by concentration, and finally by the addition of alcohol. The mother liquor contains an amorphous salt, which seems to be an isomeride of the crystallisable salt.

The amorphous salt is mixed with its own weight of potassium hydroxide, heated at 180—220° in an atmosphere of hydrogen for 20 minutes, allowed to cool, mixed with excess of dilute sulphuric acid, and distilled. The distillate contains phenol, and a larger quantity can be obtained by again heating the residue left in the retort with potassium hydroxide and again distilling. A third treatment also yields some more phenol, and the total quantity of the latter is considerable, when compared with the original quantity of acetylene. The phenol is formed by the action of the alkali on the sulphonate, and not during the action of the sulphuric acid on the acetylene (*Ann. Chim. Phys.*, [iv], **19**, 432).   C. H. B.

Derivatives of Guaiacol. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], **17**, 949—950).—*Orthonitrophenylguaiacol*, $OMe \cdot C_6H_4 \cdot O \cdot C_6H_4 \cdot NO_2$, made by the action of orthobromonitrobenzene on potassium guaiacol, forms transparent, yellow, fasciculated needles ; it melts at 55° and boils at 213° under a pressure of 10 mm.

Paranitrophenylguaiacol, $C_{13}H_{11}NO_4$, forms beautiful, yellow needles, melts at 103·5—104°, and boils at 216° under a pressure of 10 mm.

Picrylguaiacol, $OMe \cdot C_6H_4 \cdot O \cdot C_6H_2(NO_2)_3$, crystallises in yellow needles and melts at 117—118°.

Methylenediguaiacol, $(OMe \cdot C_6H_4 \cdot O)_2CH_2$, dissolves readily in the

ordinary media, with the exception of light petroleum, and forms beautiful, white crystals. It melts at 79°, and boils at 217° under 10 mm. pressure. A. L.

Ketobromides and Methylenequinones. By THEODOR ZINCKE (*J. pr. Chem.*, 1898, [ii], **58**, 441—450).—The substances obtained by the action of bromine on alkylated phenols (ketobromides) contain the bromine atom next to the alkyl group, and in the author's opinion this is the cause of the active properties of these substances, as it allows of the elimination of the elements of hydrogen bromide, with formation of methylenequinones. This, however, does not readily account for the action of acid anhydrides, and it must be presumed that hydrogen bromide is first eliminated and then immediately taken up again, but in a different position.

$$CO\underset{CBr:CBr}{\overset{CBr:CBr}{<}}>CMeBr \quad \longrightarrow \quad CO\underset{CBr:CBr}{\overset{CBr:CBr}{<}}>C:CH_2 \quad \longrightarrow$$

$$OH\cdot C\underset{CBr:CBr}{\overset{CBr\cdot CBr}{<}}>C\cdot CH_2Br,$$
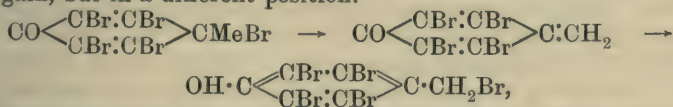
and then the anhydride reacts on this substance.

The ketobromides obtained from ortho- and para-cresol, xylenol, pseudocumenol, and parethylphenol could not be converted into methylenequinone derivatives; but paradioxydiphenylmethane gives rise to benzylidenequinone. An outline of the results obtained is given, without however, any practical details. A. W. C.

Alkyl Derivatives of Orthotoluidine. By ROBERT GNEHM and E. BLUMER (*Annalen*, 1898, **304**, 87—115).—According to Weinberg's observations, the monalkylic orthotoluidines behave as if the alkylic group wandered from the ortho-position to the amido-group. The authors' experiments indicate that the acetyl derivatives behave as if the methylic radicle occupied the para-position relatively to the amido-group. Attention has been drawn to the abnormal behaviour of these compounds by Rosenstiehl (compare Abstr., 1892, 1319), in the following terms. The methylic radicle in the ortho-position as regards nitrogen, imparts to secondary amines the properties of tertiary amines; to tertiary amines with free para-position the properties of an amine substituted in the para-position, and to a tertiary amine with a second amido-group in the para-position, the properties of an unsymmetrical alkylated diamine. The authors regard the first and second clauses of this rule as substantiated, but they cannot support the third. With the object of gaining information on this question, the following compounds have been examined.

Methylorthotoluidine *hydrochloride, hydrogen oxalate, oxalate,* and *picrate* are well-defined, crystalline salts (compare Scholl and Escales, Abstr., 1898, i, 182).

1 : 2 : 4-*Nitromethylorthotoluidine,*

$$NO_2\cdot C_6H_3Me\cdot NHMe \quad [Me:NHMe:NO_2 = 1:2:4],$$
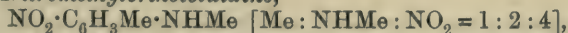
is obtained by nitrating methylorthotoluidine, methylating 4-nitrotoluidine, or by hydrolysing the product of nitrating the acetyl derivative of methylorthotoluidine; it crystallises from alcohol in red, lustrous leaflets, and melts at 107·5°. The *hydrochloride* crystallises in leaflets, and the *picrate* in prisms; the *nitroso*-derivative crystallises in yellow

needles and melts at 95°, and the *acetyl* derivative melts at 119°. The *bromo*-derivative crystallises from petrolum in brownish-yellow needles, and melts at 133°. *Nitromethylorthotoluidine*, which may have the 1 : 2 : 3-constitution, is a bye-product in the preparation of the 1 : 2 : 4 compound when 20 parts of sulphuric acid are employed in nitration ; it melts at 48°.

Orthonitro-orthotoluidineparasulphonic acid [Me : NH_2 : NO_2 : SO_3H = 1 : 2 : 3 : 5], prepared by nitrating the product of sulphonation from orthacetotoluidide, crystallises from water in slender, yellow needles ; hydrolysis yields 1 : 2 : 3-nitrotoluidine, which melts at 95°.

Methyltolylenediamine [Me : NHMe : NH_2 = 1 : 2 : 4], obtained by reducing 1 : 2 : 4-nitromethylorthotoluidine with tin or zinc dust, is a colourless oil which boils at 273°, and forms a white, crystalline *sulphate*. Methyltolylene-blue forms a *hydrochloride*, which crystallises in leaflets with metallic lustre.

1 : 2 : 4-*Nitrodimethylorthotoluidine* [Me : NMe_2 : NO_2 = 1 : 2 : 4], prepared by nitrating dimethylorthotoluidine, forms the *hydrochloride*, which crystallises in yellow leaflets, and melts at 192° ; reduction converts it into 1 : 2 : 4-*dimethyltolylenediamine*, a yellow oil.

1 : 2 : 4-*Methylorthotoluidinesulphonic acid* [Me : NHMe : SO_3H = 1 : 2 : 4] crystallises from hot water in anhydrous leaflets soluble in water to the extent of 1·76 parts in 100 at 15° ; lead peroxide, in presence of acetic acid, develops an intense blue coloration, and fused potash converts it into an amidocresol. The *sodium* salt forms leaflets, and the *barium* salt, which is indistinctly crystalline, contains $3H_2O$. The *barium* salt of the acetyl derivative forms anhydrous prisms.

Another *methylorthotoluidinesulphonic acid*, prepared by heating methylorthotoluidine with 3 parts of sulphuric acid monhydrate at 180—210° during 10 hours, crystallises in white, anhydrous needles, and develops a reddish-violet coloration with lead peroxide.

Dimethyldiamidodi-orthotolylmethane, $CH_2(C_6H_3Me\cdot NHMe)_2$, produced on passing hydrogen chloride into formaldehyde mixed with methylorthotoluidine (2 mols.), crystallises from water in reddish-violet leaflets, and melts at 87°.   M. O. F.

Chlorophenetidines, Bromophenetidines, and Nitrophenetidines, and Azo-colouring Matters derived therefrom. By FRÉDÉRIC REVERDIN and FRANZ DÜRING (*Ber.*, 1899, **32**, 152—167).— With the purpose of gaining further information relative to the influence of substituent radicles on the shade of the colouring matters derived from diazotisable amines, the authors have prepared the following derivatives of phenetidine.

Parachlororthamidophenetoil [OEt : NH_2 : Cl = 1 : 2 : 4], obtained on reducing orthonitroparachlorophenetoil with stannous chloride and hydrochloric acid, melts at 42°, and is volatile in steam ; it develops a bluish-green coloration with ferric chloride, and gives a yellowish-green precipitate with potassium dichromate. The *picrate* forms yellow, silky needles, and melts and decomposes at 132·5° ; the *sulphate* dissolves readily in alcohol and water, and the *acetyl* derivative crystallises from dilute alcohol in lustrous leaflets melting at 110°. The base is also obtained by treating acetorthamidophenetoil

with sodium chlorate and hydrochloric acid in acetic acid solution, the product being subsequently hydrolysed.

Dichloroparamidophenetoil, $C_8H_9ONCl_2$, prepared by chlorinating phenacetin and hydrolysing the product with boiling, concentrated hydrochloric acid, crystallises from dilute alcohol in prisms, and melts at 63·5—64·5°; the *acetyl* derivative, which is the direct product, crystallises from alcohol in white needles, and melts at 162°. The *sulphate* forms white leaflets, and the *picrate*, long, yellow needles, melting at 149—150°. *Orthochloroparaphenacetin* is a bye-product in the chlorination of phenacetin; it melts at 132°.

Orthochloroparamidophenetoil [OEt : Cl : NH_2 = 1 : 2 : 4], obtained on reducing orthochloroparanitrophenetoil, crystallises from dilute alcohol in small, white needles, and melts at 66°; the *picrate* and acetyl derivative (orthochloroparaphenacetin) melt at 167—170° and 132° respectively. Orthochloroparamidophenetoil is also produced by chlorinating phenacetin and hydrolysing the product (compare Hodurek, Abstr., 1897, i, 276).

Parachlorometamidophenetoil [OEt : NH_2 : Cl = 1 : 3 : 4], prepared by reducing parachlorometanitrophenetoil with tin and hydrochloric acid, remains liquid at − 12°; the *acetyl* derivative and *picrate* melt at 106° and 111° respectively.

2 : 5-*Chloronitrophenetoil*, OEt·$C_6H_3Cl·NO_2$, crystallises from petroleum in pale yellow needles, and melts at 64°. Reduction with tin and hydrochloric acid gives rise to a hydrochloride which is readily oxidised.

Orthobromoparamidophenetoil [OEt : Br : NH_2 = 1 : 2 : 4] has been prepared by Hodurek (*loc. cit.*); the picrate melts at 178—179°.

Parabromorthamidophenetoil [OEt : NH_2 : Br = 1 : 2 : 4], produced in the form of its acetyl derivative by the action of bromine and caustic soda on orthophenacetin, is very volatile in steam, and crystallises from dilute alcohol in white needles melting at 53°; the *acetyl* derivative crystallises from 60 per cent. alcohol in lustrous leaflets, and melts at 133°, whilst the *picrate* melts and decomposes at 135—137°. Unlike orthobromoparamidophenetoil, it has no reducing action on alcoholic silver nitrate, and the sulphate dissolves in sulphuric acid.

When parabromophenetoil is treated with nitric acid (2 parts) of sp. gr. = 1·485, at − 10°, it is converted into Städel's 2 : 4-bromonitrophenetoil, which melts at 98°; this instance of the wandering of a bromine atom from the para- to the ortho-position under the influence of nitric acid is comparable with the behaviour of parabromanisoil (Reverdin, Abstr., 1897, i, 27). Bye-products in this action are Körner's 2 : 4 : 6-bromodinitrophenol, Varda's tribromophenetoil, and an oil yielding parabromorthamidophenetoil on reduction.

Paranitro-orthamidophenetoil [OEt : NH_2 : NO_2 = 1 : 2 : 4], prepared by nitrating acetorthamidophenetoil (orthophenacetin) and hydrolysing the product, crystallises from dilute alcohol in orange needles or yellow leaflets, and melts at 97°; the *acetyl* derivative melts at 196°.

Metanitro-orthamidophenetoil [OEt : NH_2 : NO_2 = 1 : 2 : 5] is obtained in the form of its acetyl derivative when the operation is carried out at 25—40° instead of at 0°; it crystallises from dilute alcohol in deep yellow needles, and melts at 90°. The *acetyl* derivative melts at 165°.

A supplement to the paper contains a report supplied by the Höchst Colour Works on the character of certain dyes, to which the foregoing bases give rise.   M. O. F.

Reduction of Acylamines to Alkylamines. By THOMAS B. BAILLIE and JULIUS TAFEL (*Ber.*, 1899, **32**, 68—77).—The oxygen atom of a carbonyl group to which an amido-group is attached, can, in many cases, be replaced by hydrogen by electrolytic reduction in strong sulphuric acid solution. In this way, benzamide, benzodimethylamide, acetanilide, acetorthotoluidide, acetyltetrahydroquinoline, and benzoylpiperidine have been respectively reduced to benzylamine, benzyldimethylamine, ethylaniline, ethylorthotoluidine, ethyltetrahydroquinoline boiling at 256—258°, and benzylpiperidine. In some cases, the yields are good, in others poor, and in most cases the best conditions for the reduction have not been worked out.

When succanil (10 grams) is dissolved in concentrated sulphuric acid (90 grams) and water (10 grams), and electrolysed at 50° with a current of 5 ampères for 9 hours, 40 per cent. sulphuric acid being employed at the anode, a good yield of phenylpyrrolidone (Anschutz and Beavis, Abstr., 1897, i, 364) is obtained.

Deoxycaffeine, $\begin{matrix} NMe \cdot CH_2 \cdot C \cdot NMe \\ | \quad\quad || \\ CO-NMe-C---N \end{matrix}\!\!\!>\!\!CH$, or $\begin{matrix} NMe \cdot CO-C \cdot NMe \\ | \quad\quad || \\ CH_2 \cdot NMe \cdot C---N \end{matrix}\!\!\!>\!\!CH$,

is obtained when caffeine (1 part) dissolved in sulphuric acid (2·5 parts) and water (2·5 parts), is electrolysed with lead electrodes and a current of 15 ampères, 50 per cent. sulphuric acid being employed at the anode, and the temperature kept at 20—30°; the product of reduction is poured into water, neutralised with lime, filtered, evaporated under reduced pressure, and extracted with chloroform, the deoxycaffeine being deposited when the chloroform is evaporated. It is freed from caffeine by dissolving it in hydrochloric acid, extracting this solution several times with chloroform to remove caffeine, rendering alkaline, and again extracting with chloroform, finally crystallising the product from ethylic acetate. It crystallises with $1H_2O$, melts at 118° or, when anhydrous, at 147—148°, distils undecomposed at 245—248° under a pressure of 15—16 mm., and dissolves readily in cold alcohol, water, chloroform, or acetone. It is readily oxidised by sulphuric acid, but not by Fehling's solution, and its aqueous solution decolorises potassium permanganate and readily absorbs bromine. The *hydrochloride*, $C_8H_{12}N_4O + HCl$; *mercurichloride*, $C_8H_{12}N_4O + 2HgCl_2$; *platinochloride*, and *picrate*, $C_{14}H_{15}N_7O_8$, melting and decomposing at 194—195°, have been prepared. Acetamide, acetylpiperidine, and 2-methylpyrrolidone could not be reduced by this process.
                                                                              J. J. S.

Nitrosoacylamines. By CARL PAAL and H. APITZSCH (*Ber.*, 1899, **32**, 78—80).—*Benzylnitrosoacetamide*, $CH_2PhAc \cdot NO$, is obtained when gaseous nitrous acid is passed into a solution of pure benzylacetamide in a small quantity of acetic acid ; it is extracted with ether, and then forms a thick oil, which has not been obtained in a crystalline form. Boiling absolute alcohol decomposes it but slowly, the decomposition being more vigorous in the presence of potassium carbonate, with

formation of benzylic ethylic ether boiling at 185°, mixed with a small quantity of an ethereal salt of benzoic acid. Normal propylic alcohol also decomposes it in the presence of potassium carbonate, yielding benzylic propylic ether boiling at 196°.

Allylamine readily reacts on the nitrosamide, yielding benzylallylamine, together with other more complex compounds.　　　J. J. S.

Non-existence of Four Phenylparatolylmethenylamidines. By HENRY L. WHEELER and T. B. JOHNSON (*Amer. Chem. J.*, 1898, **20**, 853—861).—The preparation of phenylparatolylmethenylamidine by four methods has been described by Walther (Abstr., 1897, i, 242), and by the latter in conjunction with Zwingenberger (Abstr., 1898, i, 519), each method apparently giving rise to a different product. One of the authors has previously shown, however, that only one phenylparatolylmethenylamidine exists (Abstr., 1897, i, 465); it is now proved conclusively that Walther and Zwingenberger's product, melting at 120°, prepared from paratoluidine and diphenylmethenylamidine, contained a considerable quantity of the latter in an unchanged state, and that their fourth product, melting at 132°, contained unchanged diparatolylmethenylamidine. In the case of the modifications described as melting at 98° and 102°, prepared respectively from formoparatoluidide and formanilide, Walther has assumed that the methods of formation indicate their structure, although von Pechmann has frequently pointed out that such arguments are invalid in dealing with amidines. An attempt made by the authors to prepare by Walther's method the substance melting at 98° gave a product which, after seven crystallisations from light petroleum, did not melt above 86°; an attempt to prepare the variety melting at 102° gave a product which melted at 134—135°, and apparently consisted of diparatolylmethenylamidine From the above experiments, it is concluded that, without exception, the four products obtained by Walther are merely mixtures; pure phenylparatolylmethenylamidine is stated to melt at 86°.

Phenylmethenylamidephenylimidine, $NMePh \cdot CH:NPh$ (Comstock and Wheeler, Abstr., 1892, 705), is formed on adding a mixture of methylaniline and formanilide, in molecular proportion, to an excess of phosphorus trichloride, and also by the action of methylic iodide on diphenylmethenylamidine, although in the latter case the yield is poor; it is a pale yellow oil which does not solidify at 15°, and boils at 218·5—219° under a pressure of 26 mm. The *hydrochloride*, $C_{14}H_{14}N_2,HCl$, prepared by passing dry hydrogen chloride into a petroleum solution of the base, crystallises from absolute alcohol in large, transparent rhombohedra; the *aurichloride*, $C_{14}H_{14}N_2,HAuCl_4$, separates from its alcoholic solution, on adding water, in yellow six-sided plates and melts at 145°.　　　W. A. D.

Electrolytic Preparation of Phenyl-β-hydroxylamine. By FRITZ HABER (*Zeit. Elektrochem.*, 1898, **5**, 77—78).—A solution of nitrobenzene (20 grams) in glacial acetic acid (430 c.c.) diluted to 850 c.c. is used in the cathode compartment and dilute sulphuric acid in the anode compartment, a current of 4 ampères being employed with a cathode having 50 square cm. of surface. A suitable form of

apparatus with special cooling arrangements is described.   About 7
grams of nitrobenzene yields 0·5 to 0·7 gram of phenyl-β-hydroxyl-
amine.   Orthotolylhydroxylamine can be obtained in a similar way
from orthonitrotoluene.   T. E.

Alphylhydroxylamines. By EUGEN BAMBERGER (*Chem. Centr.*,
1898, ii, 1013 ; *from Arch. Sci. phys. nat. Genève*, [iv], **6**, 386—387).—By
the action of air and water, alphylhydroxylamines are converted into
azoxy-compounds with formation of hydrogen peroxide, and these
compounds can also effect the oxidation of indigo-carmine in presence
of air.   When diazomethane acts on phenylhydroxylamine, the latter
behaves like a mixture of methylene and nitrogen, and *methylenediphenyl-
hydroxylamine*, $CH_2(NPh·OH)_2$, nitrogen, and hydrogen are formed ;
the hydrogen reduces a part of the phenylhydroxylamine to aniline.
                                                           E. W. W.

**Electrolytic Reduction of Aromatic Nitro-compounds to Azo-
and Hydrazo-compounds.** By KARL ELBS and OTTO KOPP (*Zeit. Elek-
trochem.*, 1898, **5**, 108—113).—Within a porous pot, standing in a tall
beaker, is placed an anode of platinum foil, and round it a cylinder of
nickel wire gauze.   The porous pot is filled with a cold saturated
solution of sodium carbonate, and the solution to be reduced is poured
hot into the annular cathode space where the passage of the current
causes it to boil.   Under these conditions, nitro-compounds are reduced
very rapidly to azo-compounds, the completion of the reaction being
indicated by evolution of hydrogen.   The further reduction to hydrazo-
compounds goes on more slowly, and best with a smaller current
density.   The current density (in ampères per square decimetre)
calculated on the area of one side of the gauze cathode taken as though
it were continuous, varies from 10 to 16 for the azo-compounds and from
2 to 3 for the hydrazo-compounds.   The cathode solution contains
sodium acetate (5 grams), 70 per cent. alcohol (200 c.c.), and from 10
to 20 grams of the nitro-compound ; the yields are usually from 80
to 95 per cent. of the theoretical amount.   The following compounds
have been reduced : nitrobenzene, orthonitrotoluene, paranitrotoluene,
paranitrortho-xylene, and metanitraniline.   A number of determi-
nations of the current densities at which hydrogen begins to be evolved
in solutions of nitro-compounds of different concentrations and at
different temperatures are given ; these values increase with rise of
temperature and increase of concentration.   T. E.

Electrolytic Reduction of Metanitroparatoluidine. By KARL
ELBS and B. SCHWARZ (*Zeit. Elektrochem.*, 1898, **5**, 113—115).—
Metanitroparatoluidine is reduced to metadiamidoazotoluene under
conditions similar to those described by Elbs and Kopp (preceding
abstract).   The current density must not exceed 4 to 5, otherwise
metatolylenediamine is formed.   The azo-compound is usually obtained
in orange needles melting at 142—145°.   Sometimes, however, it melts
at 132° to 133°, or at 157° to 158°.   The products of lower melting point
are converted into those of higher melting point by treatment with concen-
trated sulphuric acid.   The substances with the melting points 132—133°
and 157—158° both crystallise in two different forms.   Possibly, the

products of lower melting point are labile forms of the same substance. Metadiamidorthohydrazotoluene is obtained by reduction of the azo-compound, the yield being 40—50 per cent.; the low yield is due to the formation of metatolylenediamine, which may be obtained by distilling the solution from which the sparingly soluble hydrazo-compound has crystallised. By boiling the hydrazo-compound with an alcoholic solution of hydrochloric acid containing some sulphurous anhydride, it is converted into diamidotolidine; the free base, which forms colourless crystals melting at 176°, is but slightly affected by exposure to air and light.   T. E.

Isodiazo-compounds and their Compounds with Ethylic Acetoacetate. By CARL BÜLOW (*Ber.*, 1898, **31**, 3122—3131).— Isodiazo-compounds (nitrosamines) are supposed not to enter into direct union with a methylene group which is combined with such groups as NO_2, CO, COOH, or COOEt. Paranitrisodiazobenzene, isodiazobenzene-parasulphonic acid, &c., do, however, so unite with ethylic acetoacetate, and that in alkaline solution, in which transformation into the normal diazo-compounds is impossible; the products are identical with those obtained from ethylic acetoacetate and the diazonium salts in acetic acid solution.

Paranitrisodiazobenzenesodium (nitrosamine red, paranitrophenyl-nitrosaminesodium) mixed with ethylic acetoacetate in dilute aqueous solution made feebly alkaline with sodium carbonate or hydroxide, gives a plentiful yield of Kjellin's ethylic paranitrobenzeneazoaceto-acetate (Abstr., 1897, i, 616), $NO_2 \cdot C_6H_4 \cdot N_2 \cdot CHAc \cdot COOEt$ [the author terms this ethylic paranitranitranilineazoacetoacetate, and gives similar names to the other compounds described in this paper] after remaining for 5 hours at the ordinary temperature, and by passing carbonic anhydride into the mother liquor until the latter is but just alkaline, a further crop of crystals can be obtained. This substance is not changed when it is boiled with acetic anhydride. When it is allowed to remain with dilute, aqueous-alcoholic sodium hydroxide, violet crystals of the *disodium* salt, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot CNaAc \cdot COONa$, are deposited; these are very unstable, decomposing spontaneously into the *monosodium* salt; the same change occurs more readily on dissolving in water, with or without the addition of carbonic anhydride. When the disodium salt is dissolved in acetic acid, *paranitrobenzene-azoacetoacetic acid* is formed; this is yellow, and melts and decomposes at 217°.

Paranitrobenzeneazoacetoacetamide, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot CHAc \cdot CO \cdot NH_2$, is obtained by dissolving the ethylic salt in hot, alcoholic ammonia and allowing the solution to remain; it is yellow and melts at 225—226°; with methylamine instead of ammonia, a yellow *methylamide* melting at 189° is obtained. When the ethylic salt is left in contact with phenylhydrazine in alcoholic solution, some of the *phenylhydrazone*, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot CH(COOEt) \cdot CMe \colon N \cdot NHPh$, is formed, but much of it is converted into 1-*phenyl*-3-*methyl*-4-*paranitrobenzeneazo*-5-*pyrazolone*,

$$NO_2 \cdot C_6H_4 \cdot N_2 \cdot CH {<} {\begin{array}{l} CMe \colon N \\ CO - NPh \end{array}}.$$ This can be prepared by boiling the

mixed substances with alcohol and acetic acid; it melts at 199·5°,

has a bluish lustre, dissolves in caustic alkalis, and is not decomposed by boiling with dilute acids. When it is nitrated at 55° with concentrated nitric acid and just enough water to prevent the separation of a crystalline salt, it yields 1-*paranitrophenyl-3-methyl-4-paranitrobenzene-azo-5-pyrazolone*, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot CH \begin{subarray}{l} \text{CMe:N} \\ \diagdown \\ \text{CO—N} \cdot C_6H_4 \cdot NO_2 \end{subarray}$; this is yellow, melts above 280°, and explodes when heated quickly on platinum foil. It is also formed, in addition to paranitrobenzeneazo-acetoacetic acid, when the ethylic salt of this acid is boiled with 10 per cent. hydrochloric acid for 30 hours; presumably part of the ethylic salt undergoes a transformation into the hydrazone,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot N : CAc \cdot COOEt,$$
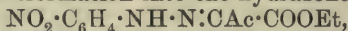
from which paranitrophenylhydrazine is then eliminated; this finally reacts with unchanged ethylic salt, forming the dinitropyrazolone.

<div align="right">C. F. B.</div>

Some Oxyazo-compounds. By MAX KRAUSE (*Ber.*, 1899, **32**, 124—127).—*Paramethoxybenzeneazophenol*, $HO \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OMe$, prepared by the action of paradiazoanisoil chloride on an alkaline solution of phenol, crystallises from dilute acetic acid in glistening, red scales, which become orange-yellow when heated to 110°, and melt at 142°; it dissolves readily in acetic acid and benzene, and less readily in chloroform. By the action of diazobenzene chloride, it is converted into *benzeneazoparamethoxybenzeneazophenol* [$OH : N_2Ph : N_2 \cdot C_6H_4 \cdot OMe = 1 : 2 : 4$]; this crystallises from dilute acetic acid in glistening, chocolate-brown needles, and melts at 117°; it dissolves readily in ether, benzene, and acetic acid, less readily in light petroleum, xylene, and chloroform, and only slightly in alcohol.

Benzeneazoparethoxybenzeneazophenol, prepared in a similar way from paradiazophenetoil, crystallises from dilute acetic acid in brownish-yellow needles and melts at 142°.

Orthomethoxybenzeneazophenol, from orthodiazoanisoil, separates from dilute acetic acid in splendid, brownish-yellow, glistening crystals, and melts at 146—147°; it is readily soluble in ether, alcohol, acetic acid, benzene, xylene, chloroform, and light petroleum. By the action of diazobenzene chloride, it is converted entirely into resinous products, as is also the corresponding ethoxy-compound.

Parachlororthobenzeneazophenol, [$OH : N_2Ph : Cl = 1 : 3 : 4$], prepared by the action of diazobenzene chloride on an alkaline solution of para-chlorophenol, crystallises from hot dilute acetic acid in fine, reddish-yellow needles melting at 110—111°; it dissolves readily in ether, alcohol, acetic acid, benzene, xylene, chloroform, and light petroleum.

The chief product of the action of nitrosobenzene on orthamidophenol is triphenodioxazine, $C_6H_4 \diagdown \begin{subarray}{l} N \\ O \end{subarray} \diagup C_6H_2 \diagdown \begin{subarray}{l} O \\ N \end{subarray} \diagup C_6H_4$, and no large amount of orthobenzeneazophenol is produced.
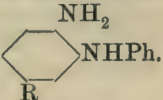
<div align="right">T. M. L.</div>

Transformation of Hydrazo-compounds Substituted in the Para-position. By PAUL JACOBSON (*Annalen*, 1898, **303**, 290—305).—It has been observed by the author that, in the case of hydrazo-compounds which are substituted in the para-position, the nature of
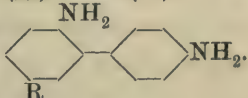
the substituent exerts a marked influence on the course of the semidine transformation (Abstr., 1893, i, 330).

When a derivative of azobenzene having one substituent in the para-position is reduced with tin and hydrochloric acid, or the hydrazo-compound formed is first isolated and then treated with acid stannous chloride, the following changes may occur. (1) Simple transformation into benzidine with elimination of the substituent.

(2) Transformation into an orthosemidine base, $\begin{array}{c} \text{NH}_2 \\ \bigcirc \text{NHPh.} \\ \text{R} \end{array}$

(3) Transformation into a parasemidine base, $\text{R}\bigcirc\text{NH}\bigcirc\text{NH}_2.$

(4) Transformation into a diphenyl base, $\begin{array}{c} \text{NH}_2 \\ \bigcirc-\bigcirc\text{NH}_2. \\ \text{R} \end{array}$

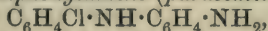(5) Resolution into aniline and a para-substituted aniline.

These five changes can occur simultaneously, as in the case of parachlorhydrazobenzene, which yields benzidine, aniline, parachlor-aniline, chlorodiamidodiphenyl, and the ortho- and para-semidine bases (following abstract); or one product preponderates, the others occurring as bye-products.

The effects of the substituents Cl, Br, I, OEt, OAc, NMe$_2$, NHAc, Me, and COOH have now been studied (succeeding abstracts) and submitted to comparison and discussion.   M. O. F.

Transformation of Parachlorhydrazobenzene. By PAUL JACOBSON and HERMANN STRÜBE (*Annalen*, 1898, **303**, 305—319).— As already stated (preceding abstract), when parachlorhydrazo-benzene is subjected to the influence of stannous chloride and hydro-chloric acid, the five possible changes occur simultaneously.

Parachloroparamidodiphenylamine (*parasemidine base*),
$$\text{C}_6\text{H}_4\text{Cl·NH·C}_6\text{H}_4\text{·NH}_2,$$
was obtained synthetically from diphenylamine, for comparison with one of the products of reducing parachlorhydrazobenzene, with which it was found to be identical; it crystallises from petroleum in colour-less leaflets, and melts at 71°. The *salicylidene* and *benzylidene* derivatives melt at 170° and 144° respectively; the *acetyl* and *diformyl* derivatives at 207° and 103° respectively, and the *thiocarbamide*, which crystallises from alcohol in lustrous leaflets, melts at 176°. 5:2:4′-*Chlorodiamidodiphenyl*, $\text{NH}_2\text{·C}_6\text{H}_3\text{Cl·C}_6\text{H}_4\text{·NH}_2$, is obtained in a purified form from the *disalicylidene* derivative, which crystallises from alcohol in needles, and melts at 166—167°; the *diacetyl* and *diformyl* derivatives melt at 204° and 194° respectively, and the *dibenzylidene* derivative melts at 104°.   M. O. F.

Transformation of Parabromhydrazobenzene. By PAUL JACOBSON and RUDOLF GROSSE (*Annalen*, 1898, **303**, 319—330).— 2:5-*Amidobromodiphenylamine* (*orthosemidine base*), $\text{NH}_2\text{·C}_6\text{H}_3\text{Br·NHPh}$, constitutes 12—15 per cent. of the product from parabromhydrazo-benzene and stannous chloride; it crystallises from benzene on adding

petroleum in colourless needles, which melt at 106° and become greyish-violet when exposed to air. When ferric chloride is added to a dilute solution of the *hydrochloride*, the liquid becomes red, and then violet, precipitating microscopic, indigo blue needles having copper reflex. The orthosemidine base is also obtained by reducing 5 : 2-*bromonitrodiphenylamine*, $NO_2 \cdot C_6H_3Br \cdot NHPh$, which crystallises from hot alcohol in reddish-brown needles and melts at 116°. The *azimide*,

$$C_6H_3Br \underset{NPh}{\overset{-N}{<}} \hspace{-6pt} \Big\rangle N,$$ separates from petroleum in silky, greyish-violet needles and melts at 126°. The *salicylidene* derivative,

$$C_6H_3Br \underset{NPh}{\overset{NH}{<}} \hspace{-6pt} \Big\rangle CH \cdot C_6H_4 \cdot OH,$$
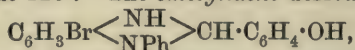
crystallises from alcohol in lustrous, sulphur-yellow needles and melts at 155°, and the *methenyl* derivative, $C_6H_3Br \underset{NPh}{\overset{-N}{<}} \hspace{-6pt} \Big\rangle CH$, in white needles which rapidly become violet ; it melts at 110°.

5 : 2 : 4'-*Bromodiamidodiphenyl*, $NH_2 \cdot C_6H_3Br \cdot C_6H_4 \cdot NH_2$, produced to the extent of 20—25 per cent. by the transformation of parabromhydrazobenzene, yields the *salicylidene* derivative, $C_{26}H_{19}N_2O_2Br$, which crystallises from petroleum and melts at 154—156° ; the *diacetyl* and *diformyl* derivatives melt at 223° and 191° respectively.

Parabromoparamidodiphenylamine, $C_6H_4Br \cdot NH \cdot C_6H_4 \cdot NH_2$, forms lustrous leaflets and melts at 79°.   M. O. F.

Transformation of Pariodohydrazobenzene. By PAUL JACOBSON, F. K. FERTSCH, and FRITZ HEUBACH (*Annalen*, 1898, **303**, 330—340). —5 : 2 : 4'-*Iododiamidodiphenyl*, $NH_2 \cdot C_6H_3I \cdot C_6H_4 \cdot NH_2$, obtained by the transformation of pariodohydrazobenzene with stannous chloride, yields the *dihydrochloride* in long, lustrous needles. The *salicylidene* derivative melts at 151°, and the *paranitrobenzylidene* derivative crystallises from benzene in yellow needles and melts at 213°.

2 : 5 : 4'-*Tri-iododiphenyl*, $C_6H_4I \cdot C_6H_3I_2$, prepared by the action of potassium iodide on diazotised iododiamidodiphenyl, separates from alcohol in brownish crystals and melts at 124—125° ; when heated with zinc dust in an atmosphere of hydrogen, it yields diphenyl.

5 : 2-*Iodoamidodiphenylamine* (*orthosemidine base*), $NH_2 \cdot C_6H_3 \cdot NHPh$, forms with benzil the *stilbazonium* [*base*, of which the *hydrochloride* crystallises from alcohol in yellow needles ; the *methenyl* compound forms white needles and melts at 161°. The base is identical with the product obtained by reducing 5 : 2-*iodonitrodiphenylamine*, $NO_2 \cdot C_6H_3I \cdot NHPh$, which crystallises from alcohol in carmine-red needles, and melts at 111°.   M. O. F.

Transformation of Paracetoxyhydrazobenzene. By PAUL JACOBSON and HERMANN TIGGES (*Annalen*, 1898, **303**, 341—352).— 2 : 4' : 5-*Diamidohydroxydiphenyl* (*hydroxydiphenyline*),

$$NH_2 \cdot C_6H_3(OH) \cdot C_6H_4 \cdot NH_2,$$
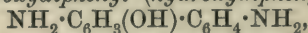
is the chief product of the action of stannous chloride on paracetoxyhydrazobenzene in presence of hydrochloric acid ; it crystallises from benzene in slender needles which quickly become coloured, and melts at 148°. This base forms the active constituent of the photographic developer " diphenal." The *salicylidene* derivative forms lustrous,

yellowish-brown leaflets and melts at 206—237°; the *anisylidene* derivative melts at 184—185°, and the *paranitrobenzylidene* derivative forms an orange powder which melts at 218°. The *diformyl* and *diacetyl* derivatives melt at 243° and 269° respectively, and the *tribenzoyl* derivative crystallises from dilute alcohol in microscopic needles, and melts at 177—178°.

Dianisylidene-ethoxydiphenyline, $C_{30}H_{28}N_2O_3$, obtained by heating the anisylidene derivative with ethylic bromide and sodium ethoxide, crystallises from alcohol in yellow needles, and melts at 124°. *Diacetylethoxydiphenyline*, $C_{18}H_{20}N_2O_3$, is prepared by the same method from the diacetyl derivative of diamidohydroxydiphenyl, and melts at 190—191°.

Ethoxydiphenyline (2 : 4′ : 5-*diamidoethoxydiphenyl*),

$$NH_2 \cdot C_6H_3(OEt) \cdot C_6H_4 \cdot NH_2,$$
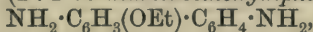
produced on hydrolysing the two foregoing substances with dilute sulphuric acid and alcoholic potash respectively, crystallises from dilute alcohol in nacreous leaflets and melts at 97°. The *hydrochloride* forms white needles, and the *dibenzoyl* derivative melts at 221°.

<div align="right">M. O. F.</div>

Transformation of Paradimethylamidohydrazobenzene. By PAUL JACOBSON and R. KUNZ (*Annalen*, 1898, **303**, 353—361. Compare Boyd, Trans., 1894, **65**, 879). — *Dimethyltriamidodiphenyl*, $C_{12}H_7(NH_2)_2 \cdot NMe_2$ [= 2 : 4′ : 5], is the chief product of the transformation of paradimethylamidohydrazobenzene, and melts at 87—89°; on adding ferric chloride to an aqueous solution of the base, an intense violet coloration is developed, rapidly becoming dark blue, and if hydrochloric acid is then added to the liquid, it becomes green, and a blue precipitate is gradually deposited. The yellow *picrate*,

$$C_{14}H_{17}N_3, 2C_6H_3N_3O_7,$$
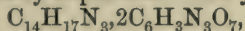
forms yellow, prismatic crystals and melts at 127°; aqueous ammonia converts this salt into the brown *picrate*, $C_{14}H_{17}N, C_6H_3N_3O_7$, which crystallises from water in reddish-brown needles and melts at 175°. The *diacetyl* derivative crystallises from dilute alcohol in small, white needles and melts at 233°. The *dibenzylidene* and *disalicylidene* derivatives melt at 146—147° and 158—159° respectively. The *thiophosgene* derivative (*dimethylamidodiphenylenethiocarbimide*),

$$NMe_2 \cdot C_{12}H_7(N \colon CS)_2,$$
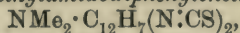
crystallises from petroleum in yellow, prismatic needles, and melts at 149°; the *thiourethane*, $C_{18}H_{19}N_3OS_2$, obtained by the action of boiling alcohol, melts at 170°.

<div align="right">M. O. F.</div>

Transformation of Paracetamidohydrazobenzene. By PAUL JACOBSON and R. KUNZ (*Annalen*, 1898, **303**, 362—367).—*Paramidoparacetamidodiphenylamine*, $NH_2 \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot NHAc$, which constitutes 15 per cent. of the product from paracetamidohydrazobenzene and stannous chloride, melts at 178°, and crystallises from hot water in lustrous, white leaflets, which become red; hydrolysis converts it into the paradiamidodiphenylamine described by Nietzki. The latter base can also be obtained in one operation by treating acetamido-

<div align="right">u 2</div>

hydrazobenzene with hydrochloric acid and stannous chloride; the *dibenzylidene* derivative melts at 182°, and the *thiocarbimide*,

$$NH(C_6H_4 \cdot N \colon CS)_2,$$
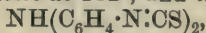
melts at 170°.   M. O. F.

Transformation of Paramethylhydrazobenzene. By PAUL JACOBSON and W. LISCHKE (*Annalen*, 1898, **303**, 367—383).—*Paramethylhydrazobenzene*, $C_6H_4Me \cdot NH \cdot NHPh$, obtained by reducing para-methylazobenzene with zinc dust and caustic soda, melts at 86—87°; and the *acetyl* and *diacetyl* derivatives at 140° and 91° respectively. The *phenylthiocarbimide* crystallises from alcohol in colourless, six-sided plates, and melts at 152°.

The orthosemidine base, produced by the transformation of para-methylhydrazobenzene, has not been obtained crystalline; the *methenyl* derivative, $C_{14}H_{12}N_2$, yields a *picrate* which melts at 195—198°, and a *mercurichloride*, which crystallises in microscopic needles and melts at 163—164°. These derivatives are identical with the compounds obtained from phenylorthotolylenediamine prepared by Schraube and Romig (Abstr., 1893, i, 340). The isomeric base, *paratolylortho-phenylenediamine*, has been recently described by O. Fischer (Abstr., 1896, i, 628); the *methenyl* compound melts at 163—164°, and the *mercurichloride* at 160°. It follows that the crude base obtained by the transformation of paramethylhydrazobenzene contains the ortho-semidine base, phenylorthotolylenediamine; the parasemidine base, paratolylparaphenylenediamine (Reichold), is also among the products.
                                                              M. O. F.

Transformation of Hydrazobenzeneparacarboxylic Acid. By PAUL JACOBSON and ADOLF STEINBRENK (*Annalen*, 1898, **303**, 384—391). —The *methylic* and *ethylic* salts of azobenzenecarboxylic acid melt at 123—124° and 85—86° respectively. *Hydrazobenzeneparacarboxylic acid*, $C_6H_5 \cdot NH \cdot NH \cdot C_6H_4 \cdot COOH$, prepared by reducing azobenzene-paracarboxylic acid in alcoholic solution with zinc dust and glacial acetic acid, crystallises from dilute alcohol in white needles and melts at 192—193°; the *methylic* salt melts at 114—115°. Benzidine is the only product of the treatment with stannous chloride which has been hitherto isolated.   M. O. F.

Symmetrical Dibenzylhydrazine. By THEODOR CURTIUS and ERWIN QUEDENFELDT (*J. pr. Chem.*, 1898, [ii], **58**, 369—392).—Some part of this work has already been noticed (Abstr., 1896, i, 28). The colourless oil obtained by exposing dibenzylhydrazine to the air crys-tallises, to some extent, after a time, but the crystals show no constant melting point. The base can be preserved in an atmosphere of carbonic anhydride without undergoing change. Acetyldibenzylhydrazine cannot be further acetylated by heating with acetic anhydride in sealed tubes.

Dibenzylhydrazine is more strongly basic than hydrazobenzene, and does not suffer rearrangement when treated with concentrated mineral acids.

Bis-azidiphenylmethane, $\begin{array}{c} CH_2Ph \cdot N \cdot N \cdot CH_2Ph \\ CH_2Ph \cdot N \cdot N \cdot CH_2Ph \end{array}$, obtained by the oxida-

tion of dibenzylhydrazine in alcoholic solution with mercuric oxide, crystallises from alcohol in beautiful, long needles melting at 152°, and is stable in presence of dilute acids or alkalis; concentrated alcoholic hydrogen chloride decomposes it into benzylideneazine and dibenzylhydrazine hydrochloride.

When preparing benzylideneazine tetrabromide, only about one-half of the theoretical yield is obtained. When kept, the filtered chloroform solution gives off hydrogen bromide, and when the chloroform has been evaporated, the red oily residue is found to consist of benzaldehyde and a *compound*, $C_{17}H_{13}N_3$, crystallising in large, colourless prisms melting at 207°; towards acids, it behaves as a weak base.

Benzylideneazine tetrabromide dissolves in alcohol with evolution of nitrogen, ethylic bromide being formed, and also a colourless, peculiar smelling oil boiling at 50° under a pressure of 15 mm., identical with the substance obtained from benzylidenic bromide and alcohol.

Benzylidenic bromide, $CHPhBr_2$, obtained by the action of phosphorus pentabromide on benzaldehyde, is a colourless, highly refractive oily liquid boiling at 156° under a pressure of 23 mm. It has a sp. gr. = 1·51 at 15°/15° and refractive index = 1·541.

Benzylideneazine monhydrochloride, $CHPh{:}N{\cdot}NCl{\cdot}CH_2Ph$, prepared by the action of hydrogen chloride on an ethereal solution of the base, forms yellow flakes melting at 150°.

Chlorine unites directly with benzylideneazine in chloroform solution, forming a *compound* crystallising from alcohol in needles melting at 57°, whilst iodine gives rise to a *compound* crystallising from alcohol in steel-blue needles melting at 150°.   A. W. C.

Formation of Chains. XXXIII. Aromatic Monacid Bases and the Bromides of α-Bromo-fatty Acids. By CARL A. BISCHOFF (*Ber.*, 1898, 31, 3236—3240).—The bromides of α-bromo-fatty acids react in the normal manner with primary and secondary aromatic amines, substituted anilides being formed. The propionyl derivatives melt at a higher temperature than the butyryl derivatives, and these again at a higher temperature than the isobutyryl derivatives, whilst these last melt at a lower temperature than the isovaleryl derivatives. The only exceptions to this rule are α-bromisobutyrylmetatoluidide and the corresponding orthonitranilide, each of which melts at a higher temperature than the corresponding butyryl derivative.

The following new compounds have been prepared in the course of the investigation.

[With TSCHUNKEW.]—*α-Bromopropionylbenzylamide*, colourless needles melting at 92°; *α-bromobutyrylbenzylamide*, long needles melting at 74°; *α-bromisobutyrylbenzylamide*, needles melting at 72°; *α-bromisovalerylbenzylamide*, silky needles melting at 98°; *α-bromisovalerylamide*, colourless plates melting at 133°.

[With PÄPKE.]—*α-Bromisovalerylorthotoluidide*, stellate groups of needles melting at 125°; *α-bromopropionylmetatoluidide*, needles melting at 80°; *α-bromobutyrylmetatoluidide*, needles melting at 79°;

a-bromisobutyrylmetatoluidide, needles melting at 91°; *a-bromisovaleryl-metatoluidide*, needles melting at 135°;; *a-bromisovalerylparatoluidide*, needles melting at 124°. *a-Bromopropionylmetaxylidide*, silky needles melting at 166°; *a-bromobutyrylmetaxylidide*, melting at 145°; *a-brom-isobutyrylmetaxylidide*, melting at 103°; *a-bromisobutyrylmetaxylidide*, melting at 153°; *a-bromisovaleryl-a-naphthalide*, melting at 172°; *a-bromisovaleryl-β-naphthalide*, melting at 145°. *a-Bromopropionyl-orthonitranilide*, fascicular groups of needles melting at 62°; *a-bromo-butyrylorthonitranilide*, needles melting at 47°; *a-bromisobutyrylortho-nitranilide*, melting at 68°; *a-bromisovalerylorthonitranilide*, melting at 52·5°.

[With WATSCHJANZ.]—*a-Bromopropionylmetanitranilide*, prismatic needles melting at 137°; *a-bromobutyrylmetanitranilide*, melting at 99°; *a-bromisobutyrylmetanitranilide*, prisms melting at 99°; *a-bromisovaleryl-metanitranilide*, prismatic needles melting at 107°.

[With HIRSCHFELD.]—*a-Bromopropionylparanitranilide*, rhombic tab-lets melting at 153°; *a-bromobutyrylparanitranilide*, short needles melting at 140°; *a-bromisobutyrylparanitranilide*, long needles melting at 123°; *a-bromisovalerylparanitranilide*, needles melting at 183°. *a-Bromisovalerylmethylanilide* has hitherto only been obtained as an oily liquid boiling at 160—163° under a pressure of 11 mm. A. H.

Formation of Chains. XXXIV. Aromatic Diacid Bases and the Bromides of *a*-Bromo-fatty Acids. By CARL A. BISCHOFF (*Ber.*, 1898, **31**, 3241—3248. Compare the foregoing abstract).— Experiments on the introduction of brominated acid radicles into diacid aromatic bases have resulted in a general confirmation of the author's theory of dynamical collisions. Hydrazobenzene, as a rule, only admits of the introduction of a single acid radicle, but does not yield an acid derivative with *a*-bromisobutyric bromide, which has no hydrogen combined with the *a*-carbon atom. *a-Bromopropionyl-diphenylhydrazide*, $NHPh \cdot NPh \cdot CO \cdot CHBrMe$, crystallises in small needles melting at 137°; *a-bromobutyryldiphenylhydrazide* forms long, pointed needles melting at 123°; *a-bromisovaleryldiphenylhydrazide* crystallises in small, colourless tablets melting at 106°. When hydrazobenzene is treated with *a*-bromisobutyric bromide, it yields azobenzene and *a*-bromisobutyrylanilide.

[With SCHATZ.]—Methylenediphenylamine does not yield any acid derivatives, substituted anilides being obtained by the action of the *a*-bromo-bromides. *Methylenediparaphenetidine*, $CH_2(NH \cdot C_6H_4 \cdot OEt)_2$, which crystallises in silky needles melting at 80°, is converted by benzoic chloride into *benzoylphenetidide* melting at 173°, and by *a*-bromo-propionic bromide into *bromopropionylphenetidide* melting at 138°.

[With PÄPKE.]—Ethylenediphenyldiamine and the corresponding orthotolyl, paratolyl, and β-naphthyl derivatives permit of the intro-duction of two acid radicles, whereas the *a*-naphthyl derivative only reacts with one molecule of the acid bromide. *Di-a-monobromiso-valerylethylenediphenyldiamine*, $C_2H_4(NPh \cdot CO \cdot CHBr \cdot CHMe_2)_2$, crystal-lises in colourless needles melting at 147°. *Di-a-monobromisovaleryl-ethylenediorthotolyldiamine* crystallises in small plates melting at

$203°$; the *paratolyl* compound melts at $109°$, and the *β-naphthyl* compound at $193°$. *α-Bromisovaleryldi-α-naphthylethylenediamine*, $CHMe_2 \cdot CHBr \cdot CO \cdot N(C_{10}H_7) \cdot CH_2 \cdot CH_2 \cdot NH \cdot C_{10}H_7$, melts at $223°$.

[With TSCHUNKEW.]—*Di-α-monobromisobutyryldi-β-naphthylethylene-diamine* crystallises in needles melting at $201°$. *Diparatolyltrimethylene-diamine*, $C_3H_6(NH \cdot C_6H_4Me)_2$, crystallises in colourless, silvery plates melting at $73°$, and readily yields diacid derivatives. The *dimono-bromopropionyl* compound melts at $127°$, and the corresponding *iso-butyryl* derivative at $113°$. A. H.

Formation of Chains. **XXXV.** Formaldehyde and Diacid Bases. By CARL A. BISCHOFF (*Ber.*, 1898, **31**, 3248—3258).—Bases of the type of those employed in the experiments described in the foregoing paper were treated with formaldehyde, in order to ascertain what conditions are favourable to the formation of ring complexes containing 2 nitrogen atoms. It was found that polymeric sub-stances are usually produced when rings containing 3 or 4 atoms might be expected, whereas rings containing 5 atoms are readily pro-duced, and no reaction occurs in cases in which the formation of a 6-atom ring might be expected. Hydrazobenzene readily reacts with formaldehyde to produce *tetraphenyldimethylenetetrazine*,
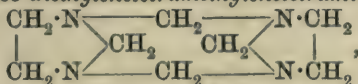
$$CH_2 \begin{array}{c} \diagup NPh \cdot NPh \diagdown \\ \diagdown NPh \cdot NPh \diagup \end{array} CH_2,$$
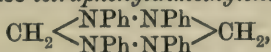
which crystallises in colourless tablets and melts at $200°$. Diphenyl-methylenediamine reacts with the aldehyde to form trimethylenetri-aniline, $NPh \begin{array}{c} \diagup CH_2 \cdot NPh \diagdown \\ \diagdown CH_2 \cdot NPh \diagup \end{array} CH_2$, melting at $143°$, accompanied by a compound which melts at $177—178°$ and is probably an isomeride or polymeride of the compound of low melting point. Three con-densation products of formaldehyde with methylenediparatoluidine have been described; diparatolyldimethylenediamine,

$$C_7H_7N \begin{array}{c} \diagup CH_2 \diagdown \\ \diagdown CH_2 \diagup \end{array} NC_7H_7,$$
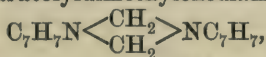
melting at $90°$ (Löb, this vol., i, 123), a polymeride of this, melting at $127—128°$ (Eibner, *ibid.*, 41), and a third substance isomeric with the latter, melting at $225—227°$; the last two compounds have the same molecular weight in boiling benzene solu-tion, and are probably geometrical isomerides of the constitution $C_7H_7 \cdot N \begin{array}{c} \diagup CH_2 \cdot N(C_7H_7) \diagdown \\ \diagdown CH_2 \cdot N(C_7H_7) \diagup \end{array} CH_2$. Ethylenediamine reacts with form-aldehyde to produce *diethylenetetramethylenetetramine*,

$$\begin{array}{c} CH_2 \cdot N \underline{\hspace{1.5em}} CH_2 \underline{\hspace{1.5em}} N \cdot CH_2 \\ | \quad \diagup CH_2 \quad CH_2 \diagdown \quad | \\ CH_2 \cdot N \underline{\hspace{1.5em}} CH_2 \underline{\hspace{1.5em}} N \cdot CH_2 \end{array},$$

which crystallises in rhombic pyramids, melts at $196°$, and boils at $250°$ with slight decomposition. Ethylenediphenylamine reacts with form-aldehyde to produce *diphenyltetrahydroglyoxaline*, $NPh \begin{array}{c} \diagup CH_2 \cdot CH_2 \\ \diagdown CH_2 \cdot NPh' \end{array}$ which crystallises in small, colourless plates, and melts at $124°$. *Diphenyldimethylethylenediamine*, melting at $165°$, was not produced in the reaction, no methylation of the secondary base by the form-

aldehyde having taken place; this base can, however, readily be prepared by the action of monomethylaniline on ethylenic bromide. Nitric acid converts the glyoxaline derivative into *dinitrosodiphenylethylenediamine* melting at 157—158°. Diparethoxydiphenylethylenediamine, when treated with formaldehyde, yields *paradiethoxydiphenyltetrahydroglyoxaline*, $OEt \cdot C_6H_4 \cdot N \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot N \cdot C_6H_4 \cdot OEt \end{smallmatrix}$, which crystallises in colourless, silvery plates melting at 214°. Diparatolyl-trimethylenediamine does not react with formaldehyde, and it was found impossible to synthesise any ring containing 2 atoms of nitrogen and 4 of carbon by the methods employed with the bases already discussed. *Malonylphenetidide*, melting at 226°, also gives no reaction with formaldehyde, whilst diparethoxydiphenylmethylenediamine is converted by formaldehyde into an open chain compound, *malonyldiphenetidide*, $CH_2(CO \cdot NH \cdot C_6H_4 \cdot OEt)_2$, melting at 226°.   A. H.

Condensation of Phthalimide with Formaldehyde. By Franz Sachs (*Ber.*, 1898, **31**, 3230—3235. Compare Abstr., 1898, i, 475).— Phthalimide readily reacts with aqueous formaldehyde at 100° to form hydroxymethylphthalimide, $C_6H_4 \colon (CO)_2 \colon N \cdot CH_2 \cdot OH$, which has previously been prepared from bromomethylphthalimide. This is converted by acetic anhydride into the *acetate*, which melts at 118°, and does not lose formaldehyde when heated. Other aldehydes do not form similar condensation products with phthalimide.

When phthalimide is brought into contact with formaldehyde and piperidine, condensation takes place, *phthalylpiperylmethylenediamine*, $C_6H_4 \colon (CO)_2 \colon N \cdot CH_2 \cdot N \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} CH_2$, being formed; this is almost insoluble in water, crystallises in long needles, melts at 117—118°, yields a yellow, sparingly soluble *picrate*, and is readily decomposed by alkalis and acids. When an alcoholic solution of phthalimide is heated at 100° with formaldehyde and piperidine, the latter acts as a reducing agent, and methylphthalimide is formed; this reaction affords a means of preparing methylamine from ammonia and formaldehyde. Tetrahydroquinoline does not appear to act in the same way as piperidine, since no methylphthalimide is obtained, a vitreous mass of unknown constitution being produced. Aqueous aniline converts both hydroxymethylphthalimide and bromomethylphthalimide into *phthalylphenylmethylenediamine*, $C_6H_4 \colon (CO)_2 \colon N \cdot CH_2 \cdot NHPh$, which crystallises in yellow, rectangular tablets; this is accompanied by a small amount of a white, sparingly soluble *substance* melting at 257°. Phenylhydrazine behaves in a similar manner to aniline, producing *phthalimidomethylenephenylhydrazine*, $C_6H_4 \colon (CO)_2 \colon N \cdot CH_2 \cdot N_2H_3Ph$, which forms yellow needles melting at 120—121°.   A. H.

Weith's Polymeric Carbodiphenylimide. By Carl Schall (*J. pr. Chem.*, 1898, [ii], **58**, 461—464).—By acting on sulphocarbanilide with boiling benzene, small amounts of triphenylguanidine and pentaphenylbiguanide are formed; after treating the partially solidified distillate with light petroleum, an oily di-imide is obtained, which solidifies when kept for some time. This substance, which shows the characteristics of Weith's polymeric carbodiphenylimide (this **Jour.**,

1876, ii, 419), melts at 168—170°, but no solvent could be found from which it could be crystallised. When heated, it is transformed into the oily *a-carbodiphenylimide*. *Acetylphenylhydrazonecarbodiphenyl-amine*, $C_{21}H_{20}N_4O$, prepared by heating a mixture of carbodiphenyl-imide and acetylphenylhydrazine, in molecular proportion, at 160—200°, crystallises from alcohol and melts at 157°. Alcoholic potash removes the acetyl group, giving rise to Marckwald and Wolff's (Abstr., 1893, i, 25) azo-base, NPh:N·C(NHPh):NPh. Bromine produces a *tribromo-derivative*, $C_{21}H_{17}Br_3N_4O$, which crystallises from glacial acetic acid and melts at 227°, with production of a red coloration.

Benzoylphenylhydrazine gives rise to the corresponding *benzoyl* derivative, separating from alcohol in white crystals melting at 110—111°. A. W. C.

Derivatives of Metahydroxybenzaldehyde. By MAX KRAUSE (*Ber.*, 1899, 32, 122—124. Compare Abstr., 1897, i, 53).—2 : 4 : 6-*Tribromometahydroxybenzaldehyde* crystallises from dilute acetic acid in yellowish-white needles and melts at 119°; the *oxime*, when crystallised from xylene or acetic acid, melts at 186°, but a small quantity of another substance melting at 226° is also produced; this appears to be an isomeric form. *Acetyl*-2 : 4 : 6-*tribromometahydroxy-benzonitrile* separates from dilute alcohol in yellowish-white, glistening flakes, and melts at 156—158°, whilst 2 : 4 : 6-*tribromometahydroxy-benzonitrile* separates from light petroleum in yellow needles and melts at 168°. 2 : 4 : 6-Tribromometahydroxybenzoic acid crystallises from hot water in long, glistening needles which have the composition $2C_7H_3Br_3O_3 + H_2O$: the anhydrous acid is insoluble in benzene and petroleum, slightly soluble in chloroform and xylene, and dissolves readily in alcohol, ether, and acetic acid; it melts at 146—147°, and is identical with the acid prepared by Werner (Abstr., 1886, 1015) by the direct bromination of metahydroxybenzoic acid; the *methylic* salt crystallises from light petroleum in flakes and needles, and melts at 119—121°.

2 : 4 : 6-*Trichlorometahydroxybenzaldehyde* crystallises from dilute acetic acid in colourless needles and melts at 115—116°; the *oxime* separates from dilute alcohol in glistening needles and melts at 170°; it dissolves readily in alcohol, ether, and acetic acid, but is only slightly soluble in benzene, xylene, chloroform, and light petroleum. *Acetyl*-2 : 4 : 6-*trichlorometahydroxybenzonitrile* separates from dilute acetic acid in glistening flakes and melts at 82—83°; 2 : 4 : 6-*trichlorometahydroxy-benzonitrile* crystallises from alcohol in yellowish, glistening needles and melts at 157°. T. M. L.

Dinitrophenyldiacetylmethane. By FERNAND MUTTELET (*Bull. Soc. Chim.*, 1897, [iii], 17, 808—809).—The hydrogen atoms of the central CH_2-group in acetylacetone can be replaced by aliphatic alkyl groups, and it was desired to ascertain whether the introduction of an aromatic radicle could be effected in a similar manner. For this purpose, 1 : 2 : 4-chlorodinitrobenzene, in which the chlorine atom possesses considerable mobility, was added to an equal weight of sodium acetylacetone dissolved in hot alcohol, and the liquid subse-quently poured into water; the oily liquid which separated was soon

converted, by agitation, into a mass of crystals melting at 121°, and only slightly soluble in cold alcohol. The crystals did not lose weight when heated at 100°, and yielded analytical results corresponding with the formula $CHAc_2 \cdot C_6H_3(NO_2)_2$. The study of this compound will be continued.   N. L.

Solubility of the Nitrobenzoic Acids. II. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1898, **17**, 329—334. Compare this vol., i, 141).—The author has previously shown that, although the solubilities of mixtures of paranitrobenzoic acid with the ortho- and with the meta-acid are those foreseen by theory, the same is not true of the solubility of a mixture of the ortho- and meta-acids; but assuming that a change in the solid phase occurs when these acids are brought together and that they no longer form a simple mixture, an explanation is afforded of their anomalous solubility. In support of this hypothesis, the following facts are adduced. (1) When a mixture of paranitrobenzoic acid with the ortho- or meta-acid is precipitated by hydrochloric acid from solution in caustic potash, its solubility is the same as that of a simple mixture of the acids in the same proportion; in the case, however, of a precipitated mixture of the ortho- and meta-acids, a considerable increase in solubility occurs. (2) Orthonitrobenzoic acid crystallises from its warm, aqueous solution in long needles, the appearance of which, under the microscope, is not changed when a considerable proportion of the para-acid is present; from a solution containing ortho- and meta-nitrobenzoic acid, however, ill-defined, arborescent crystals alone are obtained. That a change in the solid phase has here occurred is shown by the solubility in water of these crystals being different to that of the simple mixture of the acids. (3) The solubility in water of a finely pulverised mixture of paranitrobenzoic acid with either the ortho- or meta-acid is unchanged by being dissolved in ether and subsequently recovered by evaporating the solvent; when, however, a mixture of the ortho- and meta-acids is treated similarly, a considerable increase in solubility occurs.

                                                    W. A. D.

Influence of Alkalis on Optically Active Acids. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1898, **17**, 323—328).—When 10 grams of *d*-phenylglycollic acid is boiled for 17 hours with 100 c.c. of 10 per cent. aqueous potash, it is completely converted into the racemic modification; on boiling 7·6 grams of the same acid for 4 hours with 100 c.c. of normal caustic potash, only one-third, approximately, is racemised, whilst at the ordinary temperature practically no change can be detected in the rotatory power of the same solution after 66 days. Decinormal hydrochloric acid at its boiling point appears to be without action on *d*-phenylglycollic acid; at 130—135°, however, partial decomposition into benzaldehyde and formic acid occurs.

Mucic acid, when heated with caustic alkalis of various concentrations, apparently undergoes decomposition without giving rise to allomucic acid, although the latter is formed, as Fischer has shown, when a solution of mucic acid is heated with pyridine; the recognition of allomucic acid is, however, rendered difficult by its salts, both metallic

and ethereal, being ill-defined and unsuitable for microchemical detection.

Saccharic acid (9·92 grams) is largely decomposed when boiled with $2N$ caustic potash (100 c.c.) for 24 hours; it is probable that mannosaccharic acid is first formed, which is subsequently further acted on by the alkali.

Neither camphoric acid (5 grams) nor quinic acid (9·6 grams) undergo change when boiled with $2N$ caustic potash (50 c.c.) for 24 hours. From this, and the preceding experiments, it appears that the transformation of optically active compounds into their inactive forms by caustic alkalis is far from being general; the difference in the behaviour of d-tartaric acid (Abstr., 1898, i, 515, and Boeseken, *ibid.*, 561) and the compounds dealt with above, awaits explanation.

W. A. D.

Dyes from 5-Amidosalicylic Acid. By ARMIN FISCHER and F. SCHAAR-ROSENBERG (*Ber.*, 1899, 32, 81—84).—5-Amidosalicylic acid is best prepared by the following process. A solution of 290 grams of sodium nitrite in 1 litre of water is added to a solution of 500 grams of aniline hydrochloride, 600 of hydrochloric acid (sp. gr. = 1·19), and 3000 of ice, and the diazotised solution run into a solution of 533 grams of salicylic acid and 2200 grams of crystallised sodium carbonate in 10 litres of water. The yellow sodium salt of the azo-acid is separated, washed with a little water, then made into a paste with water, and added to a warm solution of 1720 grams of stannous chloride in 3500 grams of hydrochloric acid (sp. gr. = 1·19); the clear solution is treated with its own volume of concentrated hydrochloric acid, and the precipitate, consisting of the hydrochlorides of aniline and of amidosalicylic acid, separated, washed with dilute hydrochloric acid (1 : 1), dissolved in 5 litres of water, and treated with its own volume of concentrated hydrochloric acid, when a 69 per cent. yield of the nearly pure amidosalicylic acid hydrochloride is obtained.

A rhodamine dye, $C_{34}H_{22}N_2O_9$, may be obtained as follows. A finely powdered mixture of amidosalicylic acid hydrochloride (75 grams) and of fluorescein chloride (75 grams) is heated in an oil-bath at 245° for 1 hour, and then at 280° for 2 hours, when it is completely molten. The powdered melt, which consists of the compound $C_{34}H_{22}N_2O_9$ and a derivative of this obtained by the elimination of carbonic anhydride, is treated in an autoclave at 150° with an aqueous solution of 50 grams of sodium hydrogen carbonate, when the dye is obtained in solution in the form of its sodium salt. It is filtered warm, and the dye precipitated with hydrochloric acid; as all the sodium chloride cannot be removed by extraction with hot water, it is better to dry the crude product, extract the dye with alcohol, and then precipitate with water. When dried at 105°, it is a blue-violet powder, insoluble in cold and only sparingly soluble in hot water, insoluble in ether, benzene, ethylic acetate, or acetone, readily soluble in acetic acid or alcohol; its solutions in alkalis are violet, and exhibit a green fluorescence.

a-Naphthaquinoneamidosalicylic acid, $C_{10}H_5O_2 \cdot NH \cdot C_6H_3(OH) \cdot COOH$, obtained by the action of an alcoholic solution of amidosalicylic acid on *a*-naphthaquinone, crystallises from acetic acid in yellowish-red,

glistening needles, softens at 265°, and melts and decomposes at 278°, is insoluble in water or ether, sparingly soluble in alcohol or ethylic acetate ; its solutions in ammonia or sodium carbonate are claret coloured, and in sodium hydroxide blue.   J. J. S.

Camphoric Acid. V. By WILLIAM A. NOYES (*Amer. Chem. J.,* 1898, **20**, 789—814).—The author gives the following correction of melting points quoted in an earlier paper (Abstr., 1896, i, 695), the ketone from *cis*-campholytic acid, 104° (not 112—113°) ; *aa*-dimethyl-ketohexamethylene oxime, 115—117°, not 120—122° (compare Kipping, Proc., 1896, 247, and Zelinski, *Ber.,* 1897, **30**, 1543) ; and *a*-bromodihydro-*cis*-campholytic acid, 129—130° (instead of 124—125°).

It appears that 2-xylidine is best obtained in small amounts from commercial xylidine, of which it constitutes about 2 per cent. ; 2-*cyanometaxylene*, prepared from it by the Sandmeyer reaction, crystallises from light petroleum in white prisms, sublimes readily, melts at 89°, is easily soluble in alcohol and ether, and is hydrolysed only with very great difficulty.

Attempts to convert *aa*-dimethylketohexamethylene (Kipping, Trans., 1895, 351) into hexahydro-1 : 6-dimethylbenzoic acid, by reducing it to the corresponding hexanol, replacing the hydroxyl by cyanogen, and hydrolysing the product, failed.

When bromine (1 mol.) is added to a solution of diethylic ethylidenediacetoacetate (Knoevenagel, Abstr., 1895, i, 51), it is completely decolorised, no hydrogen bromide being evolved ; on heating, during 10 minutes on the water-bath, the product which remains after evaporating the chloroform, and finally extracting with ether, a white powder is left undissolved consisting of 4-*hydroxy*-2 : 6-*dimethyl-benzoic acid* ; this dissolves with difficulty in water and chloroform, but more readily in alcohol, melts at 253—254°, and gives only a slight yellow coloration with ferric chloride. Hence it does not contain the hydroxyl group in the ortho-position relatively to the carboxyl, and can be considered as derived from the compound, $COOEt \cdot CH \Big\langle {}^{CMe=\!\!=\!CH}_{CHMe \cdot CH_2} \Big\rangle CO$, assumed by Knoevenagel (*loc. cit.*) to be present in the product obtained by heating diethylic ethylidenediacetoacetate with water at 140—150°. Its formation would then be analogous to that of symmetrical xylenol from 3 : 5-dimethyl-Δ^2-cyclohexenone under similar conditions (Knoevenagel, *loc. cit.*). The *ethylic* salt, which crystallises in plates or needles and melts at 98°, remains unchanged after long boiling with alcoholic potash, aqueous soda, or hydrobromic acid.

When the hydrazine compound, prepared from the bromoxylidine obtained by Genz's method (*Ber.,* 1870, **3**, 225) from 4-metaxylidine, is treated with boiling aqueous copper sulphate according to Erdmann's directions (*Darst. org. chem. Präparate,* 71), it gives rise, not to the corresponding bromometaxylene, but to 4-*chloro*-2-*bromometaxylene*, which crystallises from alcohol in white leaflets, melts at 68°, and boils at 244° ; it thus appears that Erdmann's directions for the elimination of an amido-group are seriously at fault. When, however, the amido-group is removed by other methods, a bromoxylene is obtained which,

when boiled with acetic chloride and aluminium chloride in carbon bisulphide solution, is converted into an *acetylbromometaxylene*, which melts at 33° and boils at 275—278°. Since 5-bromometaxylene yields an acetylbromoxylene which does not solidify in a freezing mixture, and since 4-bromometaxylene does not give rise to an acetyl derivative under the above conditions, it follows, by exclusion, that in Genz's bromometaxylene the bromine atom is in position 2. From Wróblewski's results, however (Abstr., 1878, 977), it would appear that the bromoxylene has the symmetrical structure.

When 5-bromometaxylene (5 grams), obtained from 5-bromo-xylidine by Sandmeyer's reaction, is boiled for three-quarters of an hour with aluminium chloride (5 grams) and acetic chloride (5 grams) in carbon bisulphide solution, it is converted into *4-acetyl-5-bromometaxylene*, which boils at 272—276°, and does not solidify in a freezing mixture. When oxidised by means of warm, alkaline potassium permanganate, this is converted into 5-*bromometaxylyl-4-glyoxylic acid*, $C_6H_2BrMe_2\cdot CO\cdot COOH$; on adding dilute sulphuric acid to the hot solution without filtering off the manganese oxides, the glyoxylic acid is converted into 6-*bromo-2 : 4-dimethylbenzoic acid*, which crystallises from alcohol in long, slender needles and melts at 183—184°. Its structure follows from its yielding 2 : 4-dimethylbenzoic acid, when reduced with zinc dust and ammonia.

*Symmetrical iodoxylene*, prepared from symmetrical xylidine, boils at 117° under a pressure of 27 mm., and at 234—235° under atmospheric pressure ; when boiled (13·3 grams) with a mixture of carbon bisulphide (55 c.c.), aluminium chloride (11 grams) and acetic chloride (9 c.c.), for ½ hour on the water-bath, in a reflux apparatus, it is largely converted into 5-*iodo-4-acetylmetaxylene*, which boils at 171° under a pressure of 25 mm., and at 295—298° with slight decomposition under atmospheric pressure. This, on oxidation with an ice-cold, alkaline solution of potassium permanganate, is converted into 5-*iodometaxylyl-4-glyoxylic acid*, $C_6H_2IMe_2\cdot CO\cdot COOH$, which separates as an oil from the filtered solution on adding acid ; the *barium* salt, $(C_{10}H_8IO_3)_2Ba + 2\frac{1}{2}H_2O$, is only sparingly soluble in hot water. When iodoxylylglyoxylic acid is oxidised by warming on the water-bath with an alkaline solution of potassium permanganate, and subsequently adding dilute sulphuric acid, it gives rise to 2 (?)-*iodo-4 : 6-dimethylbenzoic acid* and 2-*iodo-6-methylterephthalic acid*, which were separated by means of their barium salts. The first of these acids separates from alcohol in small, granular crystals, melts at 196—197°, and is converted by zinc dust and ammonia into 4 : 6-dimethylbenzoic acid ; the *barium* salt is easily soluble in water, whilst the *copper* salt, $(C_9H_8IO_2)_2Cu + nH_2O$, is only slightly soluble. A *second iodo*-4 : 6-*dimethylbenzoic acid* was also isolated, which melted at 172—173° and differed from its congeners in being more easily soluble in water, the same being true of its copper salt; its *barium* salt, $(C_9H_8IO_2)_2Ba + 6H_2O$, however, crystallises from water in needles. The free acid, like its isomeride, is converted by reduction into 4 : 6-dimethylbenzoic acid. 2-*Iodo-6-methylterephthalic acid* crystallises from water in short, slender needles, and melts at 298° ; when treated with zinc dust and ammonia, it is converted into methylterephthalic acid, which melts

at 328—330°, not at 280—283° as stated by former observers (Fittig and Laubinger, *Annalen*, 151, 276 ; Remsen and Iles, *Amer. Chem. J.*, 1879, 1, 120). *Barium 2-iodo-6-methylterephthalate*, $C_9H_5IO_4Ba + 6H_2O$, rapidly effloresces, and is moderately soluble in water.

For preparing mesitylene, the author recommends a slightly modified form of Young and Orndorff's method (Abstr., 1893, i, 498),which gives much better results than those hitherto obtained. Acetylmesitylene, prepared by Meyer and Molz's method (*Ber.*, 1897, 30, 1271), boils at 240—241°, not at 235° as stated by Claus (Abstr., 1890, 981) ; when oxidised by an alkaline solution of potassium permanganate, it is converted into mesitylglyoxylic acid, which is transformed, on adding dilute sulphuric acid to the oxidising mixture, into trimethylbenzoic acid. On now adding the calculated quantity of alkaline potassium permanganate solution, subsequently warming, and finally adding sufficient sodium hydrogen sulphite to dissolve the precipitated manganese oxides, 2 : 6-*dimethylterephthalic acid* remains undissolved, whilst 3 : 5-*dimethylphthalic acid* passes into solution ; the latter, when heated above its melting point, is converted into the *anhydride*, $C_{10}H_8O_3$, which crystallises from light petroleum in slender, white needles and melts at 116°. 4-*Monomethylic* 2 : 6-*dimethylterephthalate* crystallises from water or alcohol in needles, and melts at 189—190° ; 2 : 6-*dimethylterephthalamic acid*, $COOH \cdot C_6H_2Me_2 \cdot CO \cdot NH_2$, prepared from it by the action of ammonia, crystallises from water in white needles, melts at 246°, and is converted by Hofmann's reaction into 4-*amido-2 : 6-dimethylbenzoic acid*, which crystallises from water in needles, and melts and decomposes at 194—195°. The *hydrochloride* is sparingly soluble in water ; by evaporating its solution in hydrochloric acid to dryness on the water-bath, it is converted into 5-metaxylidine. 4-*Iodo-2 : 6-dimethylbenzoic acid*, prepared from the amido-acid, is easily reduced by zinc dust and 10 per cent. aqueous ammonia to 2 : 6-dimethylbenzoic acid, which crystallises from light petroleum in white needles and melts at 116°, not at 97—99° as stated by Jacobsen (*Ber.*, 1878, 11, 21).   W. A. D.

Benzylpyruvic Acid. By WILHELM WISLICENUS (*Ber.*, 1898, 31, 3133—3136).—The author has compared this acid,

$$CH_2Ph \cdot CH_2 \cdot CO \cdot COOH,$$
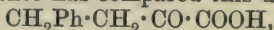
as prepared by him by boiling ethylic benzyloxalacetate with 10 per cent. sulphuric acid for a day (Abstr., 1898, i, 299) with a sample obtained by Fittig by boiling phenylhydroxycrotonic acid with 5 per cent. caustic soda (*ibid.*, 196). The acid prepared by the first method is now found to give no coloration with ferric chloride when it has been purified by repeated boiling with dilute sulphuric acid. The acid does lose its water of crystallisation, $1\frac{1}{2}H_2O$, without any liquefying when placed over sulphuric acid in an exhausted desiccator *in the dark* ; if exposed to light, it melts and volatilises slightly, but apparently undergoes no other change.   C. F. B.

Action of Ethylic Chloroglyoxylate on Aromatic Hydrocarbons. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], 17, 940—943. Compare Abstr., 1897, i, 530, and 1898, i, 585).—*Ethylic paraxylylglyoxylate* is obtained by treating purified paraxylene with

ethylic chloroglyoxylate and aluminium chloride in the usual manner; it is a colourless liquid and boils at 155—156° under a pressure of 10 mm.

Paraxylylglyoxylic acid, which melts sharply at 75° (compare Claus, Abstr., 1885, 1136), evolves carbonic oxide when heated with sulphuric acid at 100°, yielding paraxylylcarboxylic acid, and when heated with aniline gives rise to 2:5-*dimethylbenzylidineaniline*, $C_6H_3Me_2 \cdot CH:NPh$, which melts at 44°, boils at 177° (corr.) under a pressure of 10 mm. and dissolves readily in organic solvents. 2:5-*Dimethylbenzaldehyde*, $C_9H_{10}O$, is a colourless liquid having an odour of bitter almonds, and boils at 100° under 10 mm. pressure; the *hydrazone*, $N_2(:CH \cdot C_6H_3Me_2)_2$, forms magnificent, yellow needles, melts at 124°, and is sparingly soluble in alcohol.

When a mixture of ethylic chloroglyoxylate and paracymene is treated with aluminium chloride, elimination of carbonic anhydride and carbonic oxide occurs and several products are formed. *Ethylcymene*, $C_{12}H_{18}$, is a colourless liquid having an odour of cymene, and boils at 97° under a pressure of 10 mm. and at 205° under atmospheric pressure. *Ethylic cymylglyoxylate*, $C_{14}H_{18}O_3$, boils at 180° under a pressure of 10 mm.; *cymylglyoxylic acid* was obtained as a liquid, and is probably a mixture of the two possible isomerides, as, on distillation, it yielded a mixture of aldehydes and a cymylcarboxylic acid which did not crystallise. *Cymophenone*, $CO(C_{10}H_{13})_2$, is a yellowish liquid which boils at 220° under a pressure of 10 mm.

When the foregoing cymylglyoxylic acid is heated with aniline, decomposition occurs, and the resulting phenylimide boils at 210° under a pressure of 10 mm.; the latter affords a mixture of aldehydes which boils at 120° under a pressure of 10 mm., and on treatment with hydrazine hydrate gives a small quantity of a crystalline hydrazone melting at 133°, the rest of the product being oily. When boiled with potash, the aldehydes yield a mixture of the corresponding alcohols and acids; the mixed alcohols boil at 128° under a pressure of 10 mm., whilst the acids, on fractional distillation, give a considerable quantity of a substance boiling at 170° which is identical with Claus' cymylcarboxylic acid [Me : Pr : COOH = 1 : 4 : 2] and melts at 69°.

<div align="right">A. L.</div>

Glyoxylic Acids and Aldehydes Derived from Phenylic Ethers. By Louis Bouveault (*Bull. Soc. Chim.*, 1897, [iii], **17**, 943—947).—Ethylic chloroglyoxylate reacts energetically with anisoil in presence of aluminium chloride, giving a liquid which boils at 183° under a pressure of 20 mm., and consists of a mixture of *ethylic para*- and *meta-methoxyphenylglyoxylates*, $C_{11}H_{12}O_4$, the former being present in predominating amount.

Paramethoxyphenylglyoxylic acid, $OMe \cdot C_6H_4 \cdot CO \cdot COOEt$, is easily obtained from the product of hydrolysis of the above mixture of ethereal salts; it forms beautiful needles, is sparingly soluble in boiling water, readily soluble in alcohol and ether, and less readily in benzene; when anhydrous, it melts at 93°; it yields anisic acid (m. p. = 184°) when distilled.

The presence of *metamethoxyglyoxylic acid* in the mother liquors was proved by treating the mixed acids with hydrazine sulphate and decomposing the hydrazone acids by means of heat; in this way, a mixture of the *hydrazones* of anisaldehyde and metamethoxybenzaldehyde was obtained. The former is nearly insoluble in alcohol and sparingly soluble in cold benzene, crystallises in beautiful, yellow leaflets, and melts at 166—167°, whereas the latter is more readily soluble and forms beautiful, yellow crystals melting at 141°.

Ethylic   3 : 4-dimethoxyphenylglyoxylate, $C_6H_3(OMe)_2 \cdot CO \cdot COOEt$ [OMe : OMe : CO·COOEt = 3 : 4 : 1], is a somewhat viscous liquid boiling at 205° under a pressure of 10 mm.; the corresponding *amylic* salt boils at 220—225° under a pressure of 10 mm. *3 : 4-Dimethoxyphenylglyoxylic acid*, $C_{10}H_{10}O_5$, crystallises from benzene in small, white crystals and melts at 135—136°; it gives pure veratric acid when heated at its melting point. Veratric aldehyde was found to boil at 154—155° under a pressure of 10 mm.; the *hydrazone*, $N_2(C_9H_{10}O_2)_2$, is insoluble in water and the ordinary neutral solvents, and forms yellow crystals melting at 190°; the *phenylimide* is a very viscous, yellow oil, and boils at 235° under 10 mm. pressure.

2 : 4-Dimethoxyphenylglyoxylic   (dimethylresorcinolglyoxylic)   acid, $C_6H_3(OMe)_2 \cdot CO \cdot COOEt$, obtained by the decomposition of the corresponding ethylic salt, crystallises from alcohol or water in small crystals which contain $1H_2O$ and melt at 65—70°; the anhydrous acid melts at 108°. By the action of aniline, it yields *2 : 4-dimethoxybenzylidineaniline*, $C_6H_3(OMe)_2 \cdot CH:NPh$, which is a thick, yellow oil boiling at 245° under a pressure of 10 mm.; it is readily decomposed with formation of *2 : 4-dimethoxybenzaldehyde* (dimethylresorcylic aldehyde), $C_6H_3(OMe)_2 \cdot COH$, which boils at 165° under a pressure of 10 mm. and melts at 68°.

Ethylic 3 : 6-dimethoxyphenylglyoxylate (dimethylhydroquinoneglyoxylate) was not isolated, but was transformed into the phenylimide of *3 : 6-dimethoxybenzaldehyde*; the aldehyde itself melts at 51° and boils at 146° under 10 mm. pressure.   A. L.

Phenolglyoxylic Acids. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], **17**, 947—949).—Simple phenols and their acidyl compounds do not react with ethylic chloroglyoxylate under the conditions employed by the author in other cases. Phenylic picrate, however, reacts with ethylic chloroglyoxylate in presence of aluminium chloride, and yields some quantity of the *picrate* of *ethylic parahydroxyphenylglyoxylate*, $C_6H_2(NO_2)_3 \cdot O \cdot C_6H_4 \cdot CO \cdot COOEt$; this is easily hydrolysed by means of potash, yielding *potassium parahydroxyphenylglyoxylate* and picrate. Free parahydroxyphenylglyoxylic acid is decomposed by heat into parahydroxybenzoic acid and the corresponding aldehyde; a better yield of the latter is obtained by using hot dimethylaniline.

When picrylguaiacol is treated in the above manner, an *acid* is produced which is very soluble in hot water, less readily in cold water, and which probably has the constitution $OMe \cdot C_6H_3(OH) \cdot CO \cdot COOH$

[OH : OMe : CO·COOEt = 3 : 4 : 1].

A. L.

Three Cases of Desmotropism. By PAUL RABE (*Ber.*, 1899, **32**, 84—90. Compare Knorr, Abstr., 1897, i, 63 ; Schiff, Abstr., 1898, i, 237, 355, 424, 464).—The author thinks that no definite conclusions can be drawn as to the composition of a mixture of desmotropic substances by conversion into derivatives by the aid of chemical reagents, and has, therefore, restricted himself to the isolation of solid desmotropic forms. The enolic forms of ethylic alkylidenebisaceto-acetates are readily isolated by adding the sodium salts to an excess of well cooled dilute sulphuric acid and extracting with ether.

The ethylic benzylidenediacetoacetate melting at 152° (compare Schiff, *loc. cit.*) is the ketonic form ; it dissolves slowly in sodium hydroxide and is insoluble in sodium carbonate. When treated with sodium ethoxide, it yields the sodium derivative, from which the enolic form can be isolated ; this melts at about 60°, but becomes transformed into the ketonic form ; it differs from the ketonic form in the deep red-violet coloration which its alcoholic solution gives with ferric chloride and in its ready solubility in ether.

The ketonic form of ethylic ethylidenediacetoacetate melts at 80°, gives no coloration in alcoholic solution with ferric chloride, and on fusion or solution readily passes into the enolic form ; the latter crystallises from alcohol in rhombic plates, and melts at 60—61°, but at the same time becomes converted into the ketonic form.

The compound obtained by Goldschmidt and Kisser (Abstr., 1887, 475) from ethylic acetoacetate and carvone probably has the ketonic constitution, as it is insoluble in sodium carbonate and gives no coloration with ferric chloride. The *enolic* form has been obtained as an oily liquid which so far has not been reconverted into the ketonic form. J. J. S.

Condensation of " Saccharin " with Phenols. By PAUL SISLEY (*Bull. Soc. Chim.*, 1897, [iii], **17**, 821—823).—It is pointed out that compounds analogous to, if not identical with, the substances obtained by Monnet and Kœtschet by the condensation of " saccharin " with phenols (this vol., i, 212), have been previously prepared and described by the author, in conjunction with Seyewetz, in their work " *La chimie des matières colorantes artificielles.*" When treated with concentrated mineral acids, the " sacchareins " of Monnet and Kœtschet lose ammonia, and yield substances identical with the " sulphureins " obtained by Remsen and by the author. Details are given of the preparation and properties of resorcinolsuphurein and tetrabromoresor-cinolsulphurein. N. L.

The Sacchareins. A Reply to Sisley. By PAUL MONNET and J. KŒTSCHET (*Bull. Soc. Chim.*, 1897, [iii], **17**, 1030—1031).—The authors claim priority over Seyewetz and Sisley in the preparation of colouring matters by the condensation of saccharin with resorcinol (compare this vol., i, 212), and state that the compounds prepared by the latter are derived from sulphobenzoic acid and not from " saccharin." T. M. L.

Preparation of Secondary Amines from Sulphonamides. By WILHELM MARCKWALD and ALBERT (FREIHERR) VON DROSTE-HUELSHOFF (*Ber.*, 1898, **31**, 3261—3266).—Secondary amines can be

prepared from unsubstituted sulphonamides by a reaction similar to that employed by Hinsberg (Abstr., 1892, 64) for their preparation from monosubstituted sulphonamides.

Benzenesulphonamide is converted by ethylenic bromide and soda, first into dibenzenesulphoethylenediamide (Abstr., 1896, i, 47), and then into *dibenzenesulphopiperazide*, $SO_2Ph\cdot N{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}N\cdot SO_2Ph$, which is very sparingly soluble in all solvents, and forms microscopic crystals melting at 282—283° (German Patents 70055 and 70056). When a monhalogen alkyl is employed, disubstituted sulphonamides are readily produced; thus paratoluenesulphonamide is converted into *paratoluenesulphodiethylamide*, which crystallises well and melts at 60°. The disubstituted amine is best obtained by heating the sulphonamide with chlorosulphonic acid, since in this way the original sulphochloride is regenerated and a disubstituted amidosulphonic acid produced which is readily decomposed by alkalis, $R\cdot SO_2\cdot NR'_2 + Cl\cdot SO_3H = R\cdot SO_2Cl + SO_3H\cdot NR'_2$; paratoluenesulphodiethylamide, when treated in this way, yields paratoluenesulphochloride and diethylamine.

Two distinct compounds are produced by the action of trimethylenic bromide on paratoluenesulphonamide in the presence of alkali. *Paratoluenesulphotrimethyleneimide*, $C_7H_7SO_2\cdot N{<}^{CH_2}_{CH_2}{>}CH_2$, crystallises in long needles melting at 120°. The trimethylenimine ring is decomposed by acids, but can be removed from the sulphonic compound by nascent hydrogen; these reactions are still under investigation.

Diparatoluenesulphobistrimethylenedi-imide,

$$\cdot C_7H_7SO_2\cdot N{<}^{CH_2\cdot CH_2\cdot CH_2}_{CH_2\cdot CH_2\cdot CH_2}{>}N\cdot SO_2\cdot C_7H_7,$$
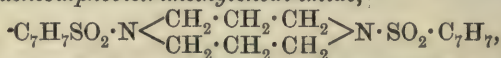
crystallises in large, silvery plates, and melts at 215°. A. H.

Hydrogenised Aromatic Compounds. By EMIL KNOEVENAGEL (*Annalen*, 1898, **303**, 259—274. Compare Abstr., 1897, i, 606).— The author has already shown that hydrogenised derivatives of toluene, metaxylene, &c., may be prepared from the 1:5-diketones which arise from condensation of ethylic acetoacetate with aldehydes of the acetic series. It is now found that if aromatic aldehydes are substituted for the compounds last named, hydrogenised derivatives of the diphenyl series are obtained.

[With J. GOLDSMITH.]—3 : 1-*Phenylmethylcyclohexanol*-5,

$$HPh{<}^{CH_2\cdot CH(OH)}_{CH_2—CHMe}{>}CH_2,$$
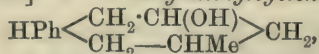
obtained by reducing phenylmethylcyclohexenone (Abstr., 1895, i, 50) in absolute alcohol with sodium, is a viscous, colourless liquid which boils at 155—159°, 166—169°, and 176—178° under pressures of 6 mm., 10 mm., and 20 mm. respectively; it has the sp. gr. = 1·024 at 18°/4°, and the refractive index $n_D = 1·5395$ at 18°. The *ether*, $C_{26}H_{34}O$, which melts at 80—100°, and boils above 300° under a pressure of 10 mm., remains in the form of a red, transparent resin when the alcohol is distilled; it has a green reflex, and is yellow when powdered. The *acetyl* derivative is a limpid oil

which boils at 173—174° and 294—297° under pressures of 10 mm. and 760 mm. respectively; it has the sp. gr. = 1·0254 at 20°/4°, and the refractive index $n_D = 1·5155$ at 20°.

3 : 1-*Phenylmethylcyclohexene*, $\quad$ CHPh$<^{CH_2 \cdot CHMe}_{CH_2 —— CH}>$CH, $\quad$ or

CHPh$<^{CH_2 \cdot CHMe}_{CH == CH}>CH_2$, prepared by heating phenylmethylcyclohexanol with phosphoric anhydride, is a limpid oil which boils at 128—130°, 146—150°, and 248—252° under pressures of 17 mm., 32 mm., and 760 mm. respectively; it has a sp. gr. = 0·9581 at 22°/4°, and the refractive index $n_D = 1·5402$ at 22°.

3 : 1-*Phenylmethylcyclohexanone*-5, CHPh$<^{CH_2 \cdot CHMe}_{CH_2 —— CO}>CH_2$, prepared by oxidising the corresponding alcohol with chromic acid, is a colourless oil which boils at 168—170° under a pressure of 16 mm.; the *oxime* separates from petroleum as a white, crystalline powder which melts at 105° (compare this vol., i, 25).
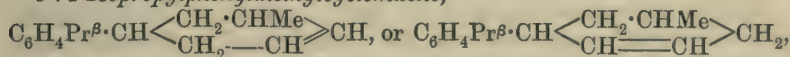
5-*Amido* 3 : 1-*phenylmethylcyclohexane*,

$$CHPh<^{CH_2 —— CHMe}_{CH_2 \cdot CH(NH_2)}>CH_2,$$
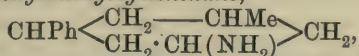
prepared by reducing the foregoing oxime with sodium in absolute alcohol, has a feeble odour of piperidine, and boils at 180—185° under a pressure of 40 mm.; the *hydrochloride* crystallises from water in lustrous leaflets and melts at 205—207°.

[With K. WEDEMEYER and F. GIESE].—3 : 1-*Isopropylphenylmethyl-cyclohexanol*-5, $C_6H_4Pr^\beta \cdot CH<^{CH_2 \cdot CH(OH)}_{CH_2 —— CHMe}>CH_2$, prepared by reducing isopropylphenylmethylcyclohexenone with sodium and absolute alcohol, boils at 185° under a pressure of 14 mm.; the *acetyl* derivative is a colourless, viscous liquid which boils at 206° under a pressure of 14 mm., and has a disagreeable odour. Treatment with glacial acetic acid saturated with hydrogen iodide converts the alcohol into a *compound* which is either the cyclohexene, $C_{16}H_{22}$, or the cyclohexane, $C_{16}H_{24}$; it boils at 153—157° under a pressure of 10 mm.

3 : 1-*Isopropylphenylmethylcyclohexene*,

$C_6H_4Pr^\beta \cdot CH<^{CH_2 \cdot CHMe}_{CH_2 —— CH}>$CH, or $C_6H_4Pr^\beta \cdot CH<^{CH_2 \cdot CHMe}_{CH == CH}>CH_2$,

arises from the foregoing alcohol under the influence of phosphoric anhydride, and boils at 149—150° under a pressure of 12 mm.; it has a sp. gr. = 0·9376 at 14°/4°, and the refractive index $n_D = 1·5283$ at 14°.

3 : 1-*Isopropylphenylmethylcyclohexanone*-5,

$$C_6H_4Pr^\beta \cdot CH<^{CH_2 \cdot CHMe}_{CH_2 —— CO}>CH_2,$$
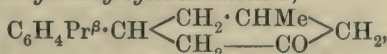
melts at 67·5° and boils at 187° under a pressure of 11 mm.; the *semicarbazone* melts at 142°. $\hfill$ M. O. F.

Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on Diphenyl in the Presence of Aluminium Chloride. By L. ROUSSET (*Bull. Soc. Chim*, 1897, [iii], 17, 809—811).—When ethylic chloroglyoxylate is added to a solution of diphenyl in boiling

carbon bisulphide containing aluminium chloride, the theoretical amount of hydrogen chloride is evolved, and *ethylic diphenylglyoxylate*, $C_6H_4Ph\cdot CO\cdot COOEt$, [is formed ; this distils at about 232° under a pressure of 9 mm., and crystallises from light petroleum in colourless plates melting at 39°. On hydrolysis, it yields *diphenylglyoxylic acid*, a colourless, crystalline substance melting at about 170°, and very soluble in the ordinary solvents. On boiling with aniline, this acid yields a *phenylimide*, which is decomposed by dilute sulphuric acid with formation of *phenylbenzaldehyde* ; this crystallises in groups of small, colourless needles, melts at 57°, boils at 184° under a pressure of 11 mm., and is very soluble in ordinary solvents, with the exception of light petroleum. The *hydrazone*, $N_2(:CH\cdot CHPh)_2$, crystallises from benzene in brilliant, yellow plates melting at about 245°. The constitution of the compounds described above is established by the fact that phenylbenzaldehyde is oxidised to paraphenylbenzoic acid by potassium permanganate in alkaline solution.

Attempts were made to introduce a 'glyoxylic residue into each of the phenyl groups in diphenyl, in order to obtain a dialdehyde, but without success.   N. L.

Compounds from Benzoic or Phthalic Chloride and Ethereal Salts of the Three Hydroxybenzoic Acids. By Heinrich Limpricht (*Annalen*, 1898, **303**, 274—289. Compare Abstr., 1896, i, 435).—When benzoic or phthalic chloride acts on an ethereal salt of orthohydroxybenzoic acid, the chlorine combines with hydrogen from the benzene ring, yielding benzoylsalicylic acid, $COPh\cdot C_6H_3(OH)\cdot COOH$, and disalicylphthalide, $CO{<}{}^{C_6H_4}_{O}{>}C[C_6H_3(OH)\cdot COOH]_2$. In the case of the meta- and para-hydroxybenzoic acids, however, it is the hydrogen of the phenolic group which suffers attack, giving rise to ethylic benzoyloxybenzoates, $COOEt\cdot C_6H_4\cdot O\cdot COPh$, and ethylic phthalyloxybenzoates, $CO{<}{}^{C_6H_4}_{O}{>}C(O\cdot C_6H_4\cdot COOEt)_2$. The general method of preparing these substances consists in heating benzoic or phthalic chloride in carbon bisulphide with aluminium chloride.

Ethylic metaphthalyloxybenzoate forms colourless, wedge-shaped, triclinic crystals, and melts at 66° ; alkalis and hydrochloric acid resolve it into metahydroxybenzoic and phthalic acids.

Ethylic parabenzoyloxybenzoate separates from ether in colourless, monoclinic crystals and melts at 89°. *Ethylic paraphthalyloxybenzoate* forms rhombic crystals and melts at 97°.

Ethylic metabenzamidobenzoate, $COPh\cdot NH\cdot C_6H_4\cdot COOEt$, melts at 114° ; hydrolysis resolves it into benzoic and amidobenzoic acids. *Ethylic metaphthalamidobenzoate*, $CO{<}{}^{C_6H_4}_{O}{>}C(NH\cdot C_6H_4\cdot COOEt)_2$, melts at 191°.

Ethylic paramidobenzoate, $NH_2\cdot C_6H_4\cdot COOEt$, separates from ether in rosettes of rhombic crystals and melts at 89° ; the *benzoyl* derivative crystallises from alcohol in white leaflets and melts at 148°. *Ethylic paraphthalamidobenzoate* separates from ethylic acetate in highly lustrous, monoclinic crystals and melts at 188° ; the *com-*

pound, $CO{<}{{}^{C_6H_4}_{O}}{>}C{:}N{\cdot}C_6H_4{\cdot}COOEt$, is produced when phthalic chloride acts on ethylic paramidobenzoate in molecular proportion.

Phthalylsalicylic acid, $COOH{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4(OH){\cdot}COOH$, results from the action of phthalic chloride on salicylic acid in carbon bisulphide under the influence of aluminium chloride; it separates from alcohol in monosymmetric crystals, and melts at 244°. The *barium* and *silver* salts are anhydrous, the former being red. *Disalicylphthalide,* which is obtained in the form of its methylic salt in association with phthalylsalicylic acid, crystallises from alcohol in slender, colourless needles and melts at 276°; hydrochloric acid at 190° resolves it into phenol, phthalic acid, and carbonic anhydride. The *barium* salt is a deep red, microscopic powder, and the *silver* salt rapidly becomes black; the *methylic* salt crystallises from alcohol in leaflets and melts at 171°. The *ethylic* salt melts at 144°.

Disalicylorthotoluic acid, $COOH{\cdot}C_6H_4{\cdot}CH[C_6H_4(OH){\cdot}COOH]_2$, prepared by reducing disalicylphthalide with zinc dust and ammonia, is precipitated by toluene from the ethereal solution as an amorphous powder; it softens at 145°, evolves gas, and then solidifies at about 152°, and subsequently fuses at 251°. The *barium* salt is a white, microcrystalline powder. M. O. F.

Syntheses by means of Phthalyl Tetrachloride (m. p. 88°). II. **Homologues of Diphenylanthrone.** [I.] By ALFRED GUYOT (*Bull. Soc. Chim.*, 1897, [iii], **17**, 966—982. Compare this vol., i, 221). —The author shows that, when ditolylphthalide is prepared by condensing phthalyl chloride with toluene, a small quantity of ditolylanthrone is also produced, on account of the presence of phthalyl tetrachloride in the commercial dichloride. The purification of the ditolylphthalide can be readily effected by dissolving it in alcoholic potash, diluting with water, and boiling the filtered solution, when the unstable potassium salt is decomposed and the phthalide reproduced; this formation of a lactone on boiling the aqueous solution is characteristic of the salts of all derivatives of phenylcarbinolorthocarboxylic acid. A better yield of ditolylphthalide is obtained by the action of aluminium chloride on the chloride of the so-called paratoluoylorthobenzoic acid, to which the author assigns the formula

$$C_6H_4Me{\cdot}C(OH){<}{{}^{C_6H_4}_{O}}{>}CO.$$
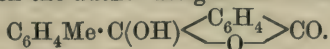
By the action of zinc dust on an alkaline solution of ditolylphthalide, *ditolylphenylmethaneorthocarboxylic acid,* $CH(C_7H_7)_2{\cdot}C_6H_4{\cdot}COOH$, is produced, and a smaller yield of the same substance can be obtained by the condensation of tolylphthalide with toluene; it melts at 172°, dissolves readily in most organic solvents, and separates from alcohol in colourless crystals; the alkali salts are very soluble in water, alcohol, and ether, and do not crystallise on evaporating the solution; the *barium* salt, $(C_{22}H_{19}O_2)_2Ba + 2\frac{1}{2}H_2O$, forms long needles. By the action of phosphorus pentachloride or of sulphuric acid, it is converted into *tolyl-3-methylanthranol,* $C_6H_4{<}{{}^{C(C_7H_7)}_{C(OH)}}{>}C_6H_3Me$; this was not analysed, but by dissolving it in acetic acid and adding potassium

dichromate it was converted directly into *tolyl-3-methyloxanthranol*, $C_6H_4 \underset{CO}{\overset{C(OH)C_7H_7}{\Big<}} \underline{\hspace{1cm}} \Big> C_6H_3Me$; the latter substance separates from toluene in slender, colourless needles, and melts at 206° ; it can be prepared directly from ditolylphthalide and phosphorus pentachloride by the author's method (*loc. cit.*), but the yield is poor.

Phenyltolylphthalide is best prepared by the condensation of toluene with the chloride of orthobenzoylbenzoic acid, $CPhCl \underset{O}{\overset{C_6H_4}{\Big<}} \underline{\hspace{0.3cm}} \Big> CO$, or of benzene with the chloride of orthotoluoylbenzoic acid,

$$C_7H_7 \cdot CCl \underset{O}{\overset{C_6H_4}{\Big<}} \underline{\hspace{0.3cm}} \Big> CO,$$
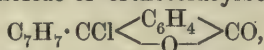
in presence of aluminium chloride. When dissolved in alcoholic potash, it is reduced by zinc dust to *diphenyltolylmethaneorthocarboxylic acid (phenyltolylorthotoluic acid)*, $C_7H_7 \cdot CHPh \cdot C_6H_4 \cdot COOH$; this, which is isomeric with the acid, $CHPh_2 \cdot C_6H_4Me \cdot COOH$, prepared by Hémilian (Abstr., 1887, 266), is also produced in smaller yield by the direct condensation of toluene with monophenylphthalide in presence of aluminium chloride ; it melts at 172°, and when distilled with anhydrous baryta under reduced pressure is converted into paratolyl-diphenylmethane. The acid obtained by Gresly (Abstr., 1886, 1035) by the action of aluminium chloride on a solution of tolylphthalide in benzene, is not identical with that just described ; the author shows that it is converted into triphenylmethane by distillation with anhydrous baryta, and that its melting point agrees with that of triphenyl-methaneorthocarboxylic acid ; its formation indicates that under the influence of the aluminium chloride the methyl group of the tolylphthalide must have been transferred to the excess of benzene used as a solvent, just as toluene is itself converted by the action of aluminium chloride into a mixture of benzene and xylene.

By the action of concentrated sulphuric acid, diphenyltolylmethane-orthocarboxylic acid is converted into *phenyl-3-methylanthranol*, $C_6H_4 \underset{COH}{\overset{CPh}{\Big<}} \Big> C_6H_3Me$, which is oxidised by potassium dichromate in acetic acid solution into phenyl-3-methyloxanthranol ; the latter can also be prepared directly from phenyltolylphthalide and phosphorus pentachloride by the author's method, but the yield is small ; it melts at 216°, and dissolves readily in ether, benzene, toluene, and acetic acid ; its constitution is established by its conversion into tolylphenyl-3-methyl-anthrone, and also by its preparation from Hémilian's diphenylpara-tolylmethaneorthocarboxylic acid [$CH_3 : COOH : CHPh_2 = 1 : 3 : 4$].

<div align="right">T. M. L.</div>

Synthesis by Means of Phthalyl Tetrachloride (m. p. 88°). II. Homologues of Diphenylanthrone. [II.] By H. GUYOT (*Bull. Soc. Chim.*, 1897, [iii], 17, 982—990).—*Phenyltolylanthrone*,

$$CO \underset{C_6H_4}{\overset{C_6H_4}{\Big<}} \Big> CPh \cdot C_7H_7,$$
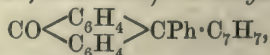
prepared by the condensation of phenyloxanthranol or its chloride with toluene, melts at 209° (corr.), and can be sublimed and distilled without decomposition ; it dissolves readily in cold benzene, toluene,

acetic acid, chloroform, and nitrobenzene, but is only sparingly soluble in alcohol, ether, or light petroleum; the molecular weight is normal.

Phenyltolyl-3-*methylanthrone*, $CO{<}{_{C_6H_3Me}^{C_6H_4}}{>}CPh \cdot C_7H_7$, prepared by the condensation of phenyloxanthranol with benzene by means of concentrated sulphuric acid, melts at 176°, sublimes without decomposition, and shows a normal molecular weight. The isomeric *ditolyl-anthrone*, $CO{<}{_{C_6H_4}^{C_6H_4}}{>}C(C_7H_7)_2$, prepared by the action of aluminium chloride on a solution of dichloranthrone (anthraquinone dichloride) in toluene, separates from nitrobenzene in large, transparent, monosymmetric prisms, of which measurements are given, and melts at 235°; it is almost insoluble in alcohol and ether, but dissolves readily in nitrobenzene, benzene, toluene, and chloroform, and shows a normal molecular weight. These two substances are isomeric with Hallgarten's dibenzylanthrone.

Ditolyl-3-*methylanthrone*, $CO{<}{_{C_6H_4Me}^{C_6H_4}}{>}C(C_7H_7)_2$, is obtained as an impurity in the preparation of ditolylphthalide from phthalyl dichloride and toluene, but is also formed by the condensation of toluene with tolyl-3-methyloxanthranol by means of sulphuric acid. The best method of preparation is, however, by the action of aluminium chloride on a mixture of phthalyl tetrachloride and toluene, in which case dichloro-3-methylanthrone and tolylchloro-3-methyl anthrone are formed as intermediate products. It also appears as a bye-product when paratoluoylorthobenzoic acid is treated with an *excess* of phosphorus pentachloride, and subsequently with toluene and aluminium chloride for the preparation of ditolylphthalide; its formation indicates that the toluoylbenzoic acid is partially converted into dichloro-3-methylanthrone, $C_6H_4{<}{_{CO}^{CCl_2}}{>}C_6H_3Me$, just as ditolylphthalide is converted by phosphorus pentachloride into tolylchloro-3-methylanthrone, $CO{<}{_{C_6H_2Me}^{C_6H_4}}{>}CCl \cdot C_7H_7$. The substance is almost insoluble in alcohol, ether, and light petroleum, but dissolves readily in chloroform, benzene, toluene, and nitrobenzene; it melts at 217°, and shows a normal molecular weight.

The author points out that, in all the cases described, condensation takes place more readily with toluene than with benzene.

T. M. L.

Two New Hydrocarbons. By PAUL COHN (*Chem. Centr.*, 1898, ii, 284; from *Österr. Chem. Zeit.*, 1, 137—138).—According to the author, a hydrocarbon, $C_{21}H_{20}$, which is probably symmetrical *triphenylpropane*, is obtained as a viscous oil of pleasant odour when 10 grams of cyclophenylenebenzylidene oxide or 10 grams of ortho-hydroxybenzhydrylamine is heated at 140—150° with 40—50 c.c. of fuming hydriodic acid and 5 grams of red phosphorus. The liquid, after shaking with ether, is made alkaline, distilled with steam, shaken with ether, and the ethereal extract evaporated. From the fractions distilling at 200—360°, of the other heavy hydrocarbons

which are formed, the author has isolated a hydrocarbon, $C_{28}H_{26}$, which is probably symmetrical *tetraphenylbutane*.   E. W. W.

Application of Schiff's Reaction to some Substituted Magentas. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, [iii], 17, 998—999). —The author has shown (Abstr., 1898, i, 568) that magenta S does not give Schiff's reaction on reducing it with sulphurous acid and then adding aldehyde ; he now shows that, whilst the homologues of magenta are very sensitive, their sulphonic acid derivatives resemble magenta S in giving no coloration when treated in this way.

                                                            T. M. L.

Transformation of Orthotolylic Carbonate into a Phthalein Derivative. By PAUL CAZENEUVE (*Compt. rend.*, 1898, 127, 1021—1023).—Orthotolylic carbonate undergoes oxidation when mixed with soda lime in the presence of atmospheric oxygen, and an aqueous extract of the product, on treatment with acid, yields an insoluble, maroon-coloured, uncrystallisable *compound* whose composition corresponds with the formula $C_{23}H_{20}O_4$. The new substance behaves like a phthalein, but has no affinity for animal and vegetable fibres ; it dissolves in ammonia and dilute alkalis. Its *acetyl* derivative is also uncrystallisable and insoluble in dilute alkalis ; in concentrated alkaline solutions, it undergoes hydrolysis, yielding the original phthalein. Guaiacol carbonate, treated in a similar manner, yields a very slight amount of colouring matter, whilst under these conditions meta- and para-tolylic carbonates undergo no change.   G. T. M.

Application of Perkin's Reaction to some Aldehydes of the Naphthalene Series. By L. ROUSSET (*Bull. Soc. Chim.*, 1897, [iii], 17, 812—816).—α-Naphthaldehyde, when heated at 180° with acetic anhydride (3 parts) and sodium acetate (1 part), yields only α-naphthyl-acrylic acid, a crystalline substance melting at 205°, which has been previously prepared by Lugli. On distillation at the ordinary pressure, this acid passes over unchanged, instead of yielding α-naphthyl-ethylene, as was expected. When heated with propionic anhydride and sodium propionate, α-naphthaldehyde yields chiefly neutral products, among which is *α-naphthylpropylene*, a liquid boiling at 137—138° under 10 mm. pressure and forming a *picrate*, $C_{10}H_7 \cdot CH\!:\!CHMe,C_6H_3N_3O_7$, which crystallises in red needles melting at 110°. There is also formed, however, a small quantity of *α-naphthylpropylenecarboxylic acid*, $C_{10}H_7 \cdot CH\!:\!CMe \cdot COOH$, which crystallises from benzene in slender, white needles melting at 151°, and is probably the first product of the reaction.

1 : 4-Methoxynaphthaldehyde reacts with acetic anhydride and sodium acetate to form 1 : 4-*methoxynaphthylacrylic acid*, a crystalline solid melting at 214°. With propionic anhydride and sodium propionate, it yields only neutral products, among which is a liquid of the formula $OMe \cdot C_{10}H_6 \cdot CH\!:\!CHMe$, which boils at 170—171° under a pressure of 9 mm., and has an odour of cloves. This substance, which may be regarded as the anethoil corresponding with naphthalene, forms a *picrate* crystallising in dark, reddish-brown needles

melting at 120°, and combines with 2 atoms of bromine to form a viscous additive product which could not be crystallised.

1 : 4-Ethoxynaphthaldehyde, when treated with propionic anhydride and sodium propionate, yields 1 : 4-*ethoxynaphthylpropylene*, OEt·C₁₀H₆·CH:CHMe, a liquid boiling at 177—178° under a pressure of 9 mm., and forming a *picrate* which crystallises in slender, reddish-brown needles melting at 137—138°.

β-Naphthaldehyde, when heated for 3 days with acetic anhydride and sodium acetate, yields a small quantity of β-*naphthylacrylic acid*, which crystallises in small grains melting at 196°. 1 : 2-Methoxynaphthaldehyde, when similarly treated, yields neither an acid nor any derivative thereof.

It appears, from these results, that Perkin's reaction is readily applicable to α-naphthaldehyde and to 1 : 4-alkyloxynaphthaldehydes, whilst it is only effected with difficulty in the case of β-naphthaldehyde, and fails altogether with 1 : 2-alkyloxynaphthaldehydes.

N. L.

Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on α-Ethoxynaphthalene in the Presence of Aluminium Chloride. By L. ROUSSET (*Bull. Soc. Chim.*, 1897, [iii], **17**, 811—812. Compare Abstr., 1898, i, 591).—Ethylic chloroglyoxylate reacts with α-ethoxynapthhalene in the presence of aluminium chloride to form *ethylic α-ethoxynaphthylglyoxylate*, which crystallises from alcohol in brilliant, white plates melting at 83°, and boiling at 240—245° under a pressure of 10 mm. On hydrolysis, it yields α-*ethoxynaphthylglyoxylic acid*, melting at 160°; and, when treated with aniline, forms a *phenylimide*, which crystallises from benzene in small, yellow grains melting at 72°. When this phenylimide is boiled with dilute sulphuric acid, it is converted into α-*ethoxynaphthaldehyde*, a crystalline solid melting at 72°. This forms a *hydrazone* which crystallises from xylene in small, yellow grains melting at 204°, and very slightly soluble in ordinary solvents. The analogy of the compounds just described with those obtained from α-methoxynaphthalene, justifies the assumption that in α-ethoxynaphthalene the entering radicle takes up the para-position with regard to the ethoxyl group. Thus, α-ethoxynaphthaldehyde has the constitution C₁₀H₆(OEt)·COH [OEt : COH = 1 : 4].

N. L.

Cryoscopic Researches in the Terpene Series. By WILHELM BILTZ (*Zeit. physikal. Chem.*, 1898, **27**, 529—551).—The molecular depressions of the freezing point were determined for solutions of a large number of compounds of the terpene series, benzene being employed as a solvent and observations being in all cases made at various concentrations. Curves representing molecular weight against depression are given, and it is seen that for all those compounds which are known to contain no hydroxyl, the curves are almost parallel to the horizontal axis, that is, the molecular weight found is almost constant, increasing but slightly with concentration. Curves of this type are given by fenchone, menthone, tanacetone, isothujone, pulegone, carvone, dihydrocarvone, citronellaldehyde, citral, cineol, and pinol. Carvenone gives a similar normal curve, and hence is most

probably ketonic, although certain of its physical properties indicate an alcoholic constitution (Abstr., 1895, i, 672). Hydroxylic compounds give curves, which rise rapidly with increase of concentration, and lead to abnormally high molecular weights (Auwers, Abstr., 1893, ii, 133; 1895, ii, 42). The curves for citronellylic alcohol and geraniol ascend rapidly, but are not quite so steep as that given by ethylic alcohol; these may be regarded as types of curves for primary alcohols. For menthol, dihydrocarveol, and *l*-borneol, which contain secondary hydroxyl, the ascent is less steep, whilst for the tertiary alcohols linalool, terpineol, *cis*-terpin (in naphthalene solution), the ascent, although evident, is still less marked. Borneol and isoborneol give different curves, that of the former being typical of a secondary alcohol, whilst that of the latter resembles those of the tertiary alcohols, although such constitution is not in accord with its chemical behaviour.   L. M. J.

Additive Compounds of Formaldehyde with Terpenes. By O. KRIEWITZ (*Ber.*, 1899, 32, 57—60).—Pinene boiling at 156—159° (20 grams), paraformaldehyde (4·4 grams), and alcohol (10 grams) are heated in sealed tubes at 170—175° for 12 hours, the contents then poured into water, and extracted with ether; a considerable quantity of terpene is recovered, and an oil boiling at 225—240° is collected separately. After purification by distillation with steam, and several fractionations, this distils at 232—236°, and has the composition $C_{11}H_{18}O$; it is a clear, somewhat viscid, strongly dextrorotatory liquid of sp. gr. = 0·961 at 20°, with an odour like that of turpentine, and is readily soluble in most organic solvents, but insoluble in water. The yield is only some 15 per cent. of the theoretical. It forms a *dihydrochloride*, $C_{13}H_{18}OCl_2$, which crystallises from light petroleum in glistening plates, melts at 74°, is optically inactive, and readily soluble in alcohol, ether, or benzene. The corresponding *dihydrobromide* melts at 77°, and the *acetyl* derivative, $C_{13}H_{20}O_2$, is a clear, colourless oil distilling at 252—256°. The *benzoyl* derivative distils at 210—215° under a pressure of 20 mm.

Dipentene, when treated in the same manner at 190—195°, yields a condensation product, $C_{11}H_{18}O$, distilling at 242—248° and having a sp. gr. = 0·9459 at 20°. Its *acetyl* derivative distils at 258—261°. Limonene also forms a condensation product, $C_{11}H_{18}O$, distilling at 246—250°, and having a sp. gr. = 0·9568 at 20°; its *acetyl* derivative boils at 259—263°.   J. J. S.

Essential Oils. By SCHIMMEL & Co. (*Chem. Centr.*, 1898, ii, 984—985; from Schimmel and Co.'s Bericht, 1898, October).—The commercial oils of citronella comprise the following two groups: (1) oils which contain 80—90 per cent. of geraniol and citronellaldehyde, have a sp. gr. = 0·886—0·894 at 15° and a rotatory power = − 0° 34' to − 2° 20', and (2) oils which contain 50—65 per cent. of geraniol and citronellaldehyde, have a sp. gr. = 0·896—0·919 at 15°, and a rotatory power = − 7° 10' to − 20° 37'. In one of the oils of the latter group having a sp. gr. = 0·915, large quantities of a camphor of specific rotatory power $[a]_D = − 55°$ were present and methyleugenol was also detected. The sp. gr. of a number of samples of dill oil

from Thuringian dill fruit varied from 0·899 to 0·911 and the rotatory power from $+76°$ to $+79°$. Unlike the English and Spanish oils, they contained only a small quantity of phellandrene.

Three samples of eucalyptus oil from Portugal were examined. The first, prepared from *Eucalyptus rostrata*, had a pleasant odour and a high content of cineol; it was soluble in 2 parts of 70 per cent. alcohol, had a sp. gr. $= 0·921$, and a specific rotatory power at $30°$ $[a]_D = -1° 8'$. The second, prepared from *Eucalyptus resinifera* (or *Eucalyptus rostrata* Schl. ?) contained cineol and phellandrene; it was insoluble in 70 or 80 per cent. alcohol, had a sp. gr. $= 0·893$, and a specific rotatory power at $30°$ $[a]_D = -17° 8'$. The third oil, prepared from *Eucalyptus obliqua* L'Herit, contained cineol and phellandrene, was soluble in an equal volume of 80 per cent. alcohol, had a sp. gr. $= 0·914$, and a specific rotatory power $[a]_D = -7° 28'$.

Portuguese oil of lavender, prepared from *Lavendula pedunculata* Cav., had an unpleasant odour and contained cineol and probably thujon; it was soluble in an equal volume of 80 per cent. alcohol, had a sp. gr. $= 0·939$, a specific rotatory power $[a]_D = -44° 54'$, and a content of ethers corresponding with 39 per cent. of linalylic acetate. Matico oils have recently been prepared which contain asarone in place of the easily crystallisable matico camphor, and also probably methyleugenol; they have a sp. gr. $= 1·077$ at $15°$ and a specific rotatory power $[a]_D = -0° 25'$.

Sandal wood oil, from *Santalum cygnorum* Miquel, has been recently distilled in Fremantle, West Australia. In order to test oil of spike for lævorotatory turpentine oils, the authors recommend the use of Ladenburg's flasks and distil 5 c.c. from 50 c.c. of oil; the distillate should have about the same dextrorotatory power as the original oil.

In determining the point of solidification of aniseed oils, a slightly modified form of Beckmann's freezing point apparatus is used.

According to the authors, Indian geranium oil contains caproic acid, and at the most only traces of citronellol, but Flatau and Labbe's fatty acid, $C_{14}H_{28}O_2$, is not present in pure oils. Moreover, Flatau and Labbe's method of separating geraniol and citronellol does not yield a pure citronellol.

Fenchene, when treated with glacial acetic acid and sulphuric acid, is converted into an isomeride of fenchylic alcohol, $C_{10}H_{18}O$, which melts at $61·5—62°$, and when oxidised yields a fenchone whose oxime melts at $82°$.

In reply to Stiehl, the authors state that lemon grass oil always contains methylheptenone and geraniol.　　　　　　　　　　　E. W. W.

Pulegenacetone. By PHILIPPE BARBIER (*Compt. rend.*, 1898, 127, 870—872).—On warming a mixture of pulegone ($1\frac{1}{2}$ mols.), ethylic acetoacetate ($\frac{1}{2}$ mol.), and glacial acetic acid (100 grams) with fused zinc chloride (75 grams) for 10 hours on the water-bath and extracting with ether, a liquid is obtained which, after the removal of unchanged pulegone and ethylic acetoacetate, boils at $148—153°$ under a pressure of 8 mm., and solidifies in the receiver; on crystalling the product from light petroleum of very low boiling point, *pulegenacetone*, $C_{13}H_{20}O$,

separates in beautiful prisms which melt at 72—73°. Its crystalline *oxime*, $C_{13}H_{21}NO$, melts at 134—135°, and yields a *benzoyl* derivative crystallising in transparent, yellow needles and melting at 178—179°. From its mode of formation, and the fact that it yields iodoform in presence of sodium hypobromite and potassium iodide, the structure of pulegenacetone is best expressed by the formula

$$\begin{array}{l} \text{CHMe·CH}_2\text{·C:CH·COMe} \\ \text{CH}_2\text{—CH}_2\text{—C:CMe}_2 \end{array}$$
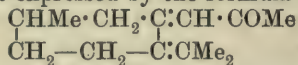
W. A. D.

The Melting Points of Some Derivatives of Amidocamphor (Correction). By OTTO MANASSE (*Ber.*, 1898, **31**, 3260. Compare Abstr., 1893, i, 479).—The melting points have been redetermined with carefully purified substances. Formamidocamphor melts at 87° (formerly stated 76—77°); acetamidocamphor melts at 121—122° (formerly stated 108°); benzamidocamphor melts at 141° (formerly stated 140°).　　　　　　　　　　　　　　　　　　　　　　A. H.

Reactions of Camphoquinone. By OTTO MANASSE and ERNST SAMUEL (*Ber.*, 1898, **31**, 3258—3260. Compare Abstr., 1898, i, 147).— When camphoquinone is treated in the cold with sulphuric acid containing 5 per cent. of sulphuric anhydride, a substance is produced which is isomeric with the quinone, and is probably its enolic form,

$$\begin{array}{l} \text{CH}_2\text{·C}\text{===}\text{C·OH} \\ \text{CMe}_2 \\ \text{CH}_2\text{·CMe·CO} \end{array}$$
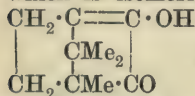
. This substance was previously obtained in small

quantities by the action of ordinary sulphuric acid on the quinone, but a much larger yield is obtained by the use of the fuming acid. When boiled with dilute sulphuric acid, it is quantitatively converted into acetone and an *acid*, $C_7H_{12}O_3$, which melts at 50—51°, and is probably a methylhydroxycyclopentanecarboxylic acid. The study of this reaction is being pursued.　　　　　　　　　　　　　　A. H.

Constitution of Camphoric Acid. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], **17**, 990—998).—The author concludes from the work of Noyes and of Walker that camphoric acid is a derivative of succinic acid containing the group ·CMe(COOH)·CH(COOH)·CH$_2$, whilst its oxidation products indicate the presence of the group :C·CMe$_2$·CMe·C: ; he therefore regards it as 1 : 1 : 2-*trimethylcyclo-pentane*-2 : 3-*dicarboxylic acid*, $\text{CH}_2\!\!\bigg\langle\begin{array}{l}\text{CMe}_2\text{·CMe·COOH}\\\text{CH}_2\text{—CH·COOH}\end{array}$.

T. M. L.

NOTE.—This formula was suggested by W. H. Perkin, jun. (Proc., 1896, 191), as an alternative to the 2 : 4-formula, but was rejected, in favour of the latter, in his recent paper (Trans., 1898, **73**, 798).

T. M. L.

Glucosides containing Caffeine and Theobromine, obtained from Plants. By C. SCHWEITZER (*Chem. Centr.*, 1898, ii, 217—218, from *Pharm. Zeit.*, **43**, 380—381. Compare Hilger, *Pharm. Zeit.*, **38**, 511).—When fresh kola nuts are extracted with chloroform, 0·613 per cent. of free caffeine, containing 1·2 per cent. of theobromine, is obtained. By treating the macerated nuts with 20 per cent. alcohol

and adding the filtrate to absolute alcohol, a ferment separates as a flocculent precipitate; kolanin is obtained from the alcoholic extract after removing the ferment and the theobromine, caffeine, sugar, salt, &c., by treating it with water containing alkali. When the alkaline extract is neutralised, the glucoside separates as a reddish, amorphous mass. By the action of the ferment or of boiling dilute sulphuric acid, kolanin yields glucose, caffeine, theobromine, and kola-red; from the quantities of the products obtained in the latter reaction kolanin may be regarded as formed by the combination of 1 mol. of kola-red with 3 mols. of glucose and 1 mol. of caffeine with elimination of 4 mols. of water, its composition would then be, $C_{40}H_{56}N_4O_{21}$. The fruit of *Theobroma Cacao* also contains theobromine and a ferment. To prepare the glucoside, cacaonin, the ferment is extracted with 20 per cent. alcohol, and the residue, after removing the fats with light petroleum, is treated with 90 per cent. alcohol. By the action of the ferment or of dilute sulphuric acid, cacaonin yields the same products as kolanin. The composition of cacaonin may perhaps be regarded as $C_{60}H_{86}O_{15}N_4$, which corresponds with that of a compound formed by the combination of 1 mol. of cacao-red, $C_{17}H_{12}(OH)_{10}$, with 6 mols. of glucose and 1 mol. of theobromine with loss of $8H_2O$.   E. W. W.

Two New Desmotroposantonins. By AMERICO ANDREOCCI and P. BERTOLO (*Ber.*, 1898, **31**, 3131—3133).—Santonin has the following specific rotations, $[a]_D$, in the solvents named; in nitric acid of sp. gr. 1·33, $-246°$ at $30°$; in sulphuric acid of sp. gr. 1·82, $-409°$ at $27°$, of sp. gr. 1·68, $-361°$ at $27°$; in phosphoric acid of sp. gr. 1·697, $-325°$ at $27°$.

When santonin is warmed with $1\frac{1}{2}$ times its volume of dilute sulphuric acid at 50—60°, it is converted into *lævodesmotroposantonin*, $C_{15}H_{18}O_3$. This melts at 194°, and has the specific rotation $[a]_D = -139°$ at 28° in absolute alcoholic solution; reduction with zinc powder and acetic acid converts it into dextrosantonous acid; it yields a *monacetyl* derivative which melts at 154°, and has the specific rotation $[a]_D = -122·9°$ at 27° in absolute alcoholic solution; when heated with ethylic iodide and sodium ethoxide, it forms an *ethyl* derivative, which melts at 82°, has the specific rotation $[a]_D = -129·3°$ at 27°, shows the characters both of a phenol and of a lactone, and is reduced by zinc powder and acetic acid to dextroethylsantonous acid, $C_{15}H_{19}O_2 \cdot OEt$. This lævodes-motroposantonin resembles the dextrorotatory isomeride melting at 189° in physical properties other than rotatory power, and an even closer resemblance exists between the acetyl and ethyl derivatives of these two substances; they unite to form racemic compounds.

Racemic desmotroposantonin is best obtained by hydrolysing the racemic acetyl derivative with caustic potash; it melts at 198°, its *acetyl* and *ethyl* derivatives at 145° and 106° respectively; zinc and acetic acid reduce it to racemic santonous acid.   C. F. B.

A New Crystalline Substance Present in Wormwood. By ADRIAN and AUGUSTE TRILLAT (*Compt. rend.*, 1898, **127**, 874—876). —On evaporating an alcoholic extract of *Artemisia Absinthium*, after removal of the absinthin, and treating the residue with amylic alcohol, a pale yellow solution is obtained from which, after two or

three days, straw-coloured, prismatic needles are deposited; after being recrystallised, the *substance* thus obtained melts at 165°, and has the composition $C_{53}H_{51}O_{20}$ or $C_{52}H_{51}O_{20}$, a cyroscopic determination of the molecular weight confirming these formulæ. It is insoluble in water and ether, but dissolves in amylic alcohol, chloroform, acetone, and light petroleum; it differs from absinthin in possessing no bitter taste, is insoluble in dilute acids and alkalis, but dissolves unchanged in cold concentrated acids, although it is decomposed by them when warm; boiling concentrated alkalis decompose it, giving rise to resinous products. With its solution in acetic acid, bromine yields an unstable *compound*; ferric chloride gives a copious black precipitate, whilst iodine dissolved in aqueous potassium iodide produces a characteristic indigo-blue precipitate. The new principle of wormwood is not changed when boiled with potassium dichromate or lead peroxide in acetic acid solution; nascent hydrogen is also without action. When heated with lime, homologues of phenol are obtained. Acetic anhydride gives rise to a white *substance*, crystallising in leaflets, which contains C = 61·63, H = 5·29, O = 33·08 per cent., melts at 162—163°, and does not yield acetic acid when heated with lime; the new substance differs from the compound from which it was prepared in its behaviour with ferric chloride and iodine, and appears to be formed by internal condensation. W. A. D.

Pyridine Derivatives from Ethylic Methylacetoacetate. By A. Sachs (*Ber.*, 1899, **32**, 61—64).—Ethylic methylacetoacetate, when treated with sodium ethoxide and trimethylenic bromide according to Lipp's method (Abstr., 1897, i, 229), yields an oily mixture which cannot be hydrolysed by hydrochloric acid, but when boiled for 3 hours with potassium hydroxide (2·5 per cent.), yields ethylic alcohol, *methylacetobutylic alcohol*, $CHMeAc \cdot [CH_2]_3 \cdot OH$, and its *anhydride*, $C_7H_{12}O$, which are best separated by distillation under diminished pressure. The anhydride boils at 37° under 20 mm., or at 131° under atmospheric pressure, is a mobile oil with a strong odour of camphor, and when shaken for several days with 5 times its volume of water, yields methylacetobutylic alcohol. This is an oily liquid, practically without odour, sparingly soluble in water, and distilling at 127° under a pressure of 20 mm. When treated with hydrogen bromide, it yields the corresponding *bromide*, which distils at 112° under a pressure of 20 mm., is practically insoluble in water, and quickly undergoes decomposition. When the bromide (1 mol.) is left in contact with alcoholic ammonia (2 mols.) for 24 hours, the solution evaporated, and the residue treated with aqueous potassium hydroxide and distilled, 2 : 3-*dimethyltetrahydropyridine*, $CH_2 <^{CMe:CMe}_{CH_2 \cdot CH_2}> NH$, is obtained as a liquid with an odour of pyridine, which readily turns brown on exposure to the air, is volatile with ether, boils at 154—156°, and is extremely difficult to dehydrate. The *hydrochloride* is extremely hygroscopic, the *picrate* crystallises in yellow needles melting at 146°, the *aurichloride*, $C_7H_{14}NAuCl_4$, melts at 140°, and is reduced when warmed with water at 65°. The *mercurichloride*, $C_7H_{13}N,HCl + 5HgCl_2$, is practically insoluble in cold water and melts at 211°.

Methylamine also reacts with the bromide, yielding 1 : 2 : 3-*trimethyl-tetrahydropyridine*, $C_8H_{15}N$, which distils at 165—167°, and has an extremely disagreeable odour ; its *picrate* melts at 152°, and its *aurichloride* melts and decomposes at 158°.

A base of higher boiling point is also formed. J. J. S.

Synthetical Alkines of the Pyridine and Piperidine Series. By ALBERT LADENBURG (*Annalen*, 1898, **304**, 54—86. Compare Abstr., 1898, i, 687).—[With KRÜGEL.]—1-*Ethyl*-2-*pipecoleine*, $C_8H_{15}N$, prepared by the action of ethylamine on ω-bromobutyl methyl ketone, is a colourless, mobile oil which boils at 163°, and resinifies when exposed to air ; it has the sp. gr. = 0·8907 at 17·5°, and the refractive indices $n_D = 1·4861$ and $n_F = 1·49427$, whence the dispersion = 0·00817. The platinochloride forms rhombohedra, and melts at 198—199° ; the *mercurichloride* melts and decomposes at 212—213°.

1-*Ethyl*-2-*pipecoline*, C_5NH_9MeEt, obtained by reducing 1-ethyl-2-pipecoleine with tin and hydrochloric acid, boils at 147—148°, and has a sp. gr. = 0·8368 at 17·5° ; the refractive indices $n_D = 1·4480$ and $n_F = 1·4541$, whence the dispersion = 0·00617. The *hydrochloride* is crystalline, but hygroscopic ; the *aurichloride* and *mercurichloride* melt at 108° and 209—210° respectively.

N-*Ethyl*-α-*pipecolyl*-β-*alkine* [2-*methyl*-3-*hydroxymethyl*-1-*ethyl*-Δ₂-*te-trahydropyridine*], $OH \cdot CH_2 \cdot C_5NH_6MeEt$, arises from the action of aqueous formaldehyde on the dilute solution of 1-ethyl-2-pipecoleine, and is colourless when freshly distilled, but rapidly becomes yellow, and finally brown ; it boils at 211°, has a sp. gr. = 0·93965 at 17·5°, and the refractive indices $n_D = 1·4626$ and $n_F = 1·46864$, whence the dispersion = 0·00604. The *platinochloride* melts at 135—136°, and decomposes at 150° ; the *aurichloride* crystallises from alcohol in rhombohedra, sinters at 94°, and melts at 111°.

N-*ethyl*-α-*pipecolyl*-β-*alkine* [2-*methyl*-3-*hydroxymethyl*-1-*ethylpiper-idine*], $C_9H_{19}NO$, prepared by reducing the foregoing base with sodium and alcohol, is a colourless, viscous liquid which boils at 225·7° (corr.), and has a sp. gr. = 0·9549 at 17·5° ; the refractive indices $n_D = 1·4778$ and $n_F = 1·4844$, whence the dispersion = 0·0066. *Di-ethylpipecolylalkinium* [2-*methyl*-3-*hydroxyethyl*-1 : 1-*diethylpiperidinium*] *iodide*, obtained on gently heating an alcoholic solution of the alkine with ethylic iodide, crystallises in needles ; the *platinochloride*, *auri-chloride*, and *mercurichloride* of the chloride melt at 190°, 91—92°, and 148—149° respectively.

1-*Ethyl*-2 : 3-*ethylenepiperidine*, $C_9H_{17}N$, is formed by heating the alkine with fuming hydrochloric acid at 180—185° during 2 hours ; it has the odour of coniine, boils at 178—180°, and has a sp. gr. = 0·86818 at 17·5°. The *platinochloride*, *aurichloride*, and *mercuri-chloride* melt at 162°, 44—45°, and 82° respectively.

[With ROSENZWEIG.]—N-*Ethyl*-α-*pipecolyl*-β-*methylalkine* [2-*methyl*-1-*ethyl*-3-*hydroxyethyl*-Δ²-*tetrahydropyridine*], $OH \cdot CHMe \cdot C_5H_6MeN \cdot Et$, prepared by the action of acetaldehyde on 1-ethyl-2-pipecoleine, boils at 106—107° and 221—223° under pressures of 19—20 mm. and 754 mm. respectively ; it has a sp. gr. = 0·94935 at 21°, and remains mobile at – 20°. The *hydrochloride* is crystalline, but very hygro-

scopic; the *platinochloride, mercurichloride,* and *picrate* melt at 167°, 116°, and 180° respectively.

N-*Ethyl-α-pipecolyl-β-methylalkine* [2-methyl-1-ethyl-3-hydroxyethyl-piperidine], $C_{10}H_{21}NO$, arises from reduction of the alkine with sodium and alcohol; it is a colourless liquid having the odour of piperidine, boils at 230·5° under a pressure of 769 mm., and has a sp. gr. = 0·9417 at 30°. The *hydrochloride* is crystalline, but very hygroscopic; the *platinochloride, mercurichloride,* and *picrate* melt at 175—176°, 145°, and 145° respectively. The ethochloride forms a *platinochloride* and *mercurichloride* which melt at 205° and 130—131° respectively.

1-*Ethyl-2 : 3-propylenepiperidine,* $C_{10}H_{19}N$, prepared from the alkine by the action of fuming hydrochloric acid at 180—185°, boils at 196° under a pressure of 763 mm., and has a sp. gr. = 0·8772 at 23°; it is a yellow, viscous liquid having the odour of coniine. The *platinochloride, aurichloride,* and *mercurichloride* melt at 179°, 63°, and 84° respectively.

1-*Ethyl-3-isopropylpiperidine,* $C_{10}H_{21}N$, is probably the base obtained by reducing the alkine with tin and hydrochloric acid (compare *loc. cit.*), and forms a colourless, highly refractive liquid with the odour of coniine; it boils at 187—192° under a pressure of 743 mm., and has a sp. gr. = 0·8517 at 27°. The *aurichloride, mercurichloride,* and *picrate* melt at 73—74°, 84°, and 117° respectively. For comparison with ethylisoconiine, 1 : 3-*ethylpropylpiperidine* has been prepared by eliminating ethylic chloride from diethylconium chloride. It boils at 185—193°, and has a sp. gr. = 0·8549 at 4°; a 30 per cent. solution in absolute alcohol gave α = 8° in a 0·5-decimetre tube. The *platinochloride* and *aurichloride* melt at 95° and 110° respectively.

[With THEODOR.]—1-*Propyl-Δ²-tetrahydropicoline,* $C_9H_{17}N$, prepared from propylamine and bromobutyl methyl ketone, boils at 184° under a pressure of 768 mm., and has a sp. gr. = 0·8875 at 20°; the *platinochloride, aurichloride,* and *mercurichloride* melt at 180°, 58—59°, and 64° respectively.

1-*Propyl-2-pipecoline,* $C_9H_{19}N$, obtained by reducing 1-propyl-pipecoleïne with tin and hydrochloric acid, is a colourless liquid with the odour of coniine, and melts at 167—167·5°. The *platinochloride, picrate,* and *mercurichloride* melt at 199—200°, 113°, and 142—143° respectively.

N-*Propyl-α-pipecolyl-β-alkine* [2-methyl-3-hydroxymethyl-1-propyl-Δ²-tetrahydropyridine], $C_{10}H_{19}NO$, is formed on treating 1-propyl-2-pipe-coleïne with formaldehyde; it is a limpid liquid which boils at 225° under a pressure of 758 mm., and has a sp. gr. = 0·9256 at 20°. The *picrate* crystallises from water in small, lustrous prisms, and melts at 147°.

N-*Propyl-α-pipecolyl-β-alkine* [2-methyl-3-hydroxymethyl-1-propylpiper-idine], $C_{10}H_{21}NO$, prepared by reducing the foregoing base with sodium and alcohol, boils at 233—234·5° under a pressure of 756·2 mm., and has a sp. gr. = 0·9376 at 20°; the *platinochloride* and *mercuri-chloride* melt at 184—185° and 78° respectively.

[With BRANDT.]—N-*Methyl-α-pipecolyl-β-methylalkine* [1 : 2-dimethyl-3-hydroxyethyl-Δ²-tetrahydropyridine], $C_5NH_6Me_2 \cdot CHMe \cdot OH$, obtained

from 1-methyl-2-pipecoleine and acetaldehyde, boils at 106—109° and 206—210° under pressures of 10 mm. and 752 mm. respectively, and has a sp. gr. = 0·9418 at 24°. The *aurichloride, platinochloride, mercurichloride,* and *picrate* melt at 127°, 175—177°, 158—165°, and 194—198° respectively.

N-*Methyl-α-pipecolyl-β-methylalkine* [1 : 2-*dimethyl-3-hydroxyethylpiperidine*], formed on reducing the foregoing base with sodium and alcohol, crystallises in white needles melting at 30°; it boils at 227—229° (corr.) under a pressure of 756·8 mm., and has a sp. gr. = 0·9664 at 19°. The *platinochloride, mercurichloride,* and *picrate* melt at 197—198°, 169—171°, and 126—129° respectively.

1-*Methyl*-2 : 3-*propylenepiperidine*, $C_9H_{17}N$, is probably obtained by heating 1-methyl-2-pipecolyl-3-methylalkine with fuming hydrochloric acid at 180—190°; it is a limpid, colourless liquid, which boils at 179—184° under a pressure of 762·7 mm., and has a sp. gr. = 0·8797 at 20°. The *aurichloride, platinochloride, mercurichloride,* and *picrate* melt at 90—93°, 147—150°, 181—183°, and 108—110° respectively.

1-*Methyl-3-isopropylpiperidine*, $C_9H_{19}N$, is probably the base which is formed when the foregoing base is reduced with tin and hydrochloric acid; it is a colourless, mobile liquid, with the odour of piperidine, boils at 175—180° under a pressure of 743 mm., and has a sp. gr. = 0·8494 at 18°. The *aurichloride, platinochloride,* and *picrate* melt at 125—128°, 154—155°, and 162—163° respectively.

M. O. F.

Aromatic Urethanes of Tetrahydroquinoline. By Paul Cazeneuve and Moreau (*Compt. rend.,* 1898, **127,** 868—870).— Tetrahydroquinoline interacts with phenolic carbonates in the same manner as piperidine, conicine, and piperazine (Abstr., 1898, i, 692), giving rise to aromatic urethanes; in preparing these, it is necessary to employ an excess of the base (4 mols.), which is boiled during 2 hours with the phenolic carbonate (1 mol.).

Phenylic tetrahydroquinolineurethane, $C_9H_{10}N \cdot COOPh$, prepared by this method from phenylic carbonate, separates from alcohol of 93° in white crystals, melts at 51—52°, distils unchanged at about 300°, and is easily soluble in the usual solvents; the corresponding *orthochloro*-derivative, $C_9H_{10}N \cdot COO \cdot C_6H_4Cl$, prepared from orthochlorophenylic carbonate, closely resembles it, and melts at 61°.

The *urethane*, $C_9H_{10}N \cdot COO \cdot C_6H_4 \cdot OMe$, prepared from guaiacol carbonate and tetrahydroquinoline, crystallises from alcohol in aggregates of hard needles radiating from centres, and melts at 69°.

α-Naphthylic and *β-naphthylic tetrahydroquinolineurethanes*, prepared from α- and β-naphthylic carbonates, crystallise from alcohol, and melt at 73° and 118—119° respectively.

Attempts to prepare the tetrahydroquinolineurethanes derived from the cresols and thymol by the method given above, failed, mixed ethylic carbonates of the phenols alone being obtained (compare Cazeneuve and Morel, this vol., i, 29); the explanation of this behaviour is probably to be found in the difficulty with which the mixed alkylic and phenylic carbonates first formed undergo hydrolysis.

W. A. D.

Double Salicylates of Metals and Antipyrine. By M. C.
SCHUYTEN (*Chem. Centr.*, 1898, ii, 704 ; from *Bull. Acad. roy. Belg.*,
[iii], **35**, 836—849. Compare *Bull. Acad. roy. Belg.*, [iii], **34**, 933).—
When copper sulphate (1 mol.) is added to a dilute solution of sodium
salicylate (2 mols.) and antipyrine (1 mol.), rosette shaped clusters of
green, rhombic crystals of a *copper antipyrine salicylate*,

$$C_{11}H_{12}N_2O,(OH \cdot C_6H_4 \cdot COO)_2Cu,$$
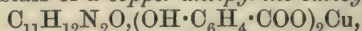
separate ; when more concentrated solutions are used, a flocculent
precipitate is formed. The double salt is slightly soluble in water and
alcohol, and melts and decomposes at 192°. As its solutions give
the ordinary reactions of copper, the metal cannot be present in the
salt as a complex ion.

Attempts to prepare double salicylates of antipyrine with silver, gold,
and mercury failed. When a dilute solution of sodium salicylate and
antipyrine is mixed with a solution of zinc chloride or zinc sulphate,
a zinc antipyrine salicylate, $(C_{11}H_{12}N_2O)_2,(OH \cdot C_6H_4 \cdot COO)_2Zn$, separates
after some time in colourless needles ; this is slightly soluble in cold,
but more soluble in warm, water, alcohol, and ether, rather soluble in
cold chloroform, and melts and decomposes at 75—76° ; the aqueous
solution has an acid reaction and gives the ordinary reactions of zinc
salts. The cadmium salt, $(C_{11}H_{12}N_2O)_2,(OH \cdot C_6H_4 \cdot COO)_2Cd$, prepared in
a similar way to the above salts, crystallises in long needles, is slightly
soluble in water, more easily in benzene and toluene, and melts
and decomposes at 95° ; its aqueous solution also gives the reactions of
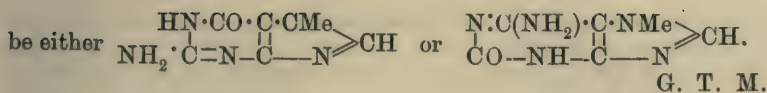cadmium salts.   E. W. W.

Homologues of Theobromine. By HEINRICH BRUNNER (*Chem.
Centr.*, 1898, ii, 474 ; from *Schweiz. Wochenschr. Pharm.*, **36**, 303—304).
—According to the author, there are two kinds of homologues of
theobromine, the true homologues which crystallise with difficulty
and melt above 270°, and derivatives of caffeine which crystallise
easily in long needles and have lower melting points. The theobromine
silver compound, when treated with methylic iodide, yields caffeine alone,
but with ethylic iodide, a crystalline powder which melts above 270°
is obtained, and also a crystalline isomeride which melts at 165°. The
latter, which remains in the mother liquor, is identical with Van der
Sloten's compound, whilst the former corresponds with Philips'
preparation (this Jour., 1877, i, 93). Propylic iodide appears only to
yield the microcrystalline modification with the higher melting point.
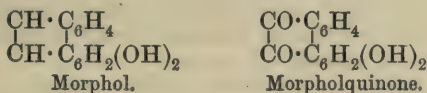   E. W. W.

Epiguanine (7-Methylguanine). By MARTIN KRÜGER and
GEORG SALOMON (*Zeit. physiol. Chem.*, 1898, **26**, 389—394).—Epi-
guanine, obtained from urine, and formerly stated to have a composi-
tion corresponding with $C_{10}H_{13}N_9O_2$ (Abstr., 1896, i, 92) is shown to
be identical with 7-methylguanine (2-amido-6-oxy-7-methylpurine)
synthesised by Fischer (Abstr., 1898, i, 98). On treatment with
nitrous acid, the base is converted into heteroxanthine (7-methyl-

xanthine), $\begin{array}{l} HN:CO \cdot C \cdot NMe \\ OC \cdot NH \cdot C \underline{\quad\quad} N \end{array} \!\!> CH$; therefore, 7-methylguanine may

be either $\underset{NH_2 \cdot C=N-C-N}{HN \cdot CO \cdot C \cdot CMe}{>}CH$ or $\underset{CO-NH-C-N}{N:C(NH_2) \cdot C \cdot NMe}{>}CH.$

<div align="right">G. T. M.</div>

Non-nitrogenous Decomposition Products of Morphine. III. By EDUARD VONGERICHTEN (*Ber.*, 1898, **31**, 2924—2925).— Acetylmethylmorpholquinone (Abstr., 1898, i, 98, 281) was digested with a solution of sodium methoxide in methyl alcohol; the methylmorpholquinone formed was liberated with sulphuric acid, suspended in water, and oxidised with excess of 4 per cent. potassium permanganate solution; from the filtered solution, the phenylhydrazone of phthalonic acid was obtained, and after acidifying and oxidising with excess of permanganate, phthalic acid was found to be present. In no experiment was any other than phthalic acid found, so that the two hydroxyl groups in morphol are attached to the same benzene nucleus; moreover, they are probably attached to adjacent carbon atoms, for Barth and Weidel showed some time ago that protocatechuic acid is formed when morphine is fused with potash. The following formulæ are, therefore, adopted.

$$\underset{\text{Morphol.}}{\underset{CH \cdot C_6H_2(OH)_2}{CH \cdot C_6H_4}} \qquad \underset{\text{Morpholquinone.}}{\underset{CO \cdot C_6H_2(OH)_2}{CO \cdot C_6H_4}}$$

<div align="right">C. F. B.</div>

Non-nitrogenous Decomposition Products of Morphine. By EDUARD VONGERICHTEN (*Ber.*, 1898, **31**, 3198—3202. Compare Abstr., 1898, i, 98, 281).—Morphenol, when distilled with zinc dust in an atmosphere of hydrogen, yields phenanthrene; and its methylic ether, when reduced with sodium and alcohol, yields a *phenol* which crystallises in needles, but readily undergoes alteration when exposed to the atmosphere; its *acetyl* derivative could not be obtained in a crystalline form, but when oxidised with an acetic acid solution of chromic anhydride, it gave acetylmethylmorpholquinone; a *benzoylmethylmorpholquinone* melting at 228° has been obtained by treating the crude phenol with benzoic chloride and oxidising. The formula suggested for morphenol is $O{<}{\underset{C_6H_2(OH)}{\overset{C-CH}{}}}{>}C_6H_4$ [C : OH : O = 2 : 4 : 5]
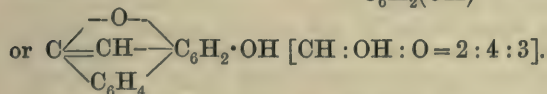
or $C{\underset{C_6H_4}{\overset{-O-}{{\Longleftarrow}CH-}}}{>}C_6H_2 \cdot OH$ [CH : OH : O = 2 : 4 : 3]. J. J. S.

Thebaine. By MARTIN FREUND [and CARL HOLTHOF] (*Ber.*, 1899, **32**, 168—196. Compare Abstr., 1897, i, 495).—*Methebenine*, $(OMe)_2 \cdot C_{16}H_{11}O \cdot NHMe$, obtained by heating thebaine (10 grams), during 2—3 hours at 100°, with methylic alcohol (15 c.c.) mixed with an equal volume of the alcohol which has been saturated with hydrogen chloride, sinters at 155°, melts at 165—167°, and is somewhat sparingly soluble in alcohol. The *hydrochloride* crystallises in aggregates of needles and melts at 245°; the *hydriodide* separates from dilute alcohol in rhombic plates, sinters at 190°, and melts at 195—198°. The *diacetyl* derivative crystallises from absolute alcohol in snow-white
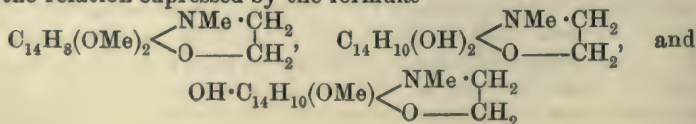
<div align="right">y 2</div>

needles, and melts at 176°; the *methylmethebenine methiodide*, produced
by the action of methylic iodide in excess, forms microscopic prisms
and melts at 215°. Methebenine is the methylic ether of thebenine,
and the latter substance is obtained from it when the hydrochloride is
heated with 20 per cent. hydrochloric acid. *Methebenol*, $C_{16}H_{10}O(OMe)_2$,
is the result of eliminating hydrogen iodide and trimethylamine from the
methinemethiodide by the agency of 15 per cent. caustic potash; it
separates from glacial acetic acid in greyish crystals and melts at
133—134°. It is identical with the substance obtained from thebenol
and methylic iodide (*loc. cit.*).

Ethebenine, $OMe \cdot C_{16}H_{11}O(OEt) \cdot NHMe$, is produced under conditions
similar to those observed in the preparation of methebenine, ethylic
alcohol being used instead of methylic alcohol; the *hydrochloride* melts at
248°, and the *hydriodide*, which crystallises from water in highly
refractive, rhombic plates containing $1H_2O$, sinters at 200° and melts
at 206—207°. The *diacetyl* derivative melts at 163°, and the
methylethebenine methiodide, which crystallises in minute, six-sided
plates, sinters at 210° and melts at 215°. *Ethebenol*, $OEt \cdot C_{16}H_{10}O \cdot OMe$,
produced when the methinemethiodide is treated with boiling alkali,
crystallises from glacial acetic acid in small, rhombic plates, and
melts at 103—105°; it is also obtained from thebenol and ethylic
iodide in presence of sodium ethoxide.

Prothebenine, $OMe \cdot C_{16}N_{11}O(OPr) \cdot NHMe$, prepared from thebaine
and propylic alcohol under the influence of hydrogen chloride, sinters
at 167° and melts at 172—173°; the *hydrochloride*, which crystallises
in microscopic, six-sided leaflets, sinters at 215° and melts at
220—221°, whilst the hydriodide forms rhombic leaflets, softens at
210°, and melts at 212—213°. The *methylprothebenine methiodide*
separates from dilute alcohol in microscopic, six-sided plates and melts
at 202°. *Prothebenol*, $OPr \cdot C_{16}H_{10}O \cdot OMe$, obtained by the action of
boiling caustic potash on the methinemethiodide, crystallises from glacial
acetic acid in rhombic plates, softens at 99°, and melts at 103—105°;
it is also produced when thebenol is heated with propylic iodide and
alcoholic sodium ethoxide.

Morphothebaine, $C_{18}H_{19}NO_3$, is the base obtained by the action of
concentrated hydrochloric or hydrobromic acid on thebaine (compare
Howard, Abstr., 1884, 1201); the formula, $C_{17}N_{17}NO_3$, ascribed to it
by Howard, is not confirmed by the author, who finds that one of the
two methoxylic groups which occur in the orginal alkaloid remains
intact. Morphothebaine crystallises from methylic alcohol in
beautiful, bluish crystals belonging to the rhombic system. The hydro-
chloride, hydrobromide, and hydriodide melt at 256—260°, 270—275°,
and 243—244° respectively; the *triacetyl* derivative, regarded by
Howard as the acetyl derivative, melts at 193—194°, whilst the
methiodide crystallises in quadratic plates and melts at 221—222°.

The fact that thebaine, morphine, and codeine stand to one another
in the relation expressed by the formulæ

$$C_{14}H_8(OMe)_2 {<}{\overset{NMe \cdot CH_2}{\underset{O \longrightarrow CH_2}{}}}, \quad C_{14}H_{10}(OH)_2 {<}{\overset{NMe \cdot CH_2}{\underset{O \longrightarrow CH_2}{}}}, \quad \text{and}$$

$$OH \cdot C_{14}H_{10}(OMe) {<}{\overset{NMe \cdot CH_2}{\underset{O \longrightarrow CH_2}{}}}$$

respectively, suggested the possibility of arriving at the dimethylic ether of morphine or the methylic ether of codeine by addition of two hydrogen atoms to thebaine. This prospect, however, has not been realised.

Dihydrothebaine, $C_{16}H_{14}O(OMe)_2 \cdot NHMe$, prepared by reducing thebaine in alcoholic solution with sodium, crystallises from a mixture of benzene and petroleum in minute, quadratic prisms, and melts at 154°. The *methiodide* crystallises from ethylic alcohol in four-sided prisms which contain 1 mol. of the solvent and melt at 155—160°; a similar form, containing 1 mol. of the solvent, separates from methylic alcohol, whilst water deposits the substance in minute needles melting at 75—80°, and containing $3H_2O$.

Isodihydrothebaine hydriodide, $OH \cdot C_{16}H_{13}ONMe_2 \cdot OMe, HI$, obtained by the action of sulphurous acid on the methiodide of dihydrothebaine, crystallises from hot water and melts at 230—235°; the *base* crystallises from benzene and melts at 138°, whilst the *methiodide* melts at 210—215°.

Isocodeine, $C_{18}H_{21}NO_3$, is the name given by the author to a substance produced when dihydrothebaine is dissolved in cold, dilute hydrochloric acid; it is a snow-white, amorphous powder which melts at 70—80°. M. O. F.

Brucine. By NICOLA MOUFANG and JULIUS TAFEL (*Annalen*, 1898, **304**, 24—49).—The authors confirm the empirical formula, $C_{23}H_{26}N_2O_4$, now ascribed to brucine, and although the alkaloid usually contains $4H_2O$ when crystallised from water, have obtained a form from this solvent containing $2H_2O$; the same modification is produced on crystallising brucine from alcohol.

Brucinic acid, $NH:C_{20}H_{20}NO(OMe)_2 \cdot COOH$, prepared by heating brucine with alcoholic sodium ethoxide at 80°, forms a crystalline powder containing $1H_2O$, and melts and decomposes at 245°; it dissolves in dilute mineral acids, which converts it into salts of brucine. Chromic acid and ferric chloride develop a transitory green coloration, and concentrated nitric acid gives a yellowish-red solution. The nitrosamine yields a *hydrochloride*, which crystallises from warm water in small needles, and melts indefinitely at 236°. The *methiodide*, which is almost insoluble in cold water, contains $1H_2O$, and melts and decomposes at 218°. The *methylbetaine* (*methylbrucine*), $C_{24}H_{30}N_2O_5$, prepared by the action of moist silver oxide on the methiodide of brucinic acid, forms yellow crystals containing $4H_2O$, which is removed at 105°; it melts and decomposes at 276°.

Nitrobrucine hydrate, $C_{21}H_{21}N_2O_3(OMe)_2 \cdot NO_2$, obtained by heating brucine with 5 per cent. nitric acid in a reflux apparatus, is precipitated by sodium acetate from aqueous solutions in lustrous, golden leaflets containing water of crystallisation, which is removed at 100°; it chars without melting when strongly heated. It is readily dissolved by dilute acids and by caustic alkalis; the solution in alkali carbonates is golden-yellow, becoming brown on treatment with caustic soda, whilst the solution in dilute ammonia also becomes brown when boiled. The *platinochloride* is crystalline, and the *mercurichloride* amorphous.

Bidemethylnitrobrucine hydrate, $C_{21}H_{21}N_2O_3(OH)_2 \cdot NO_2$, prepared

by the action of caustic soda on the nitrate (see below), is precipitated by acetic acid from alkaline solutions in reddish-yellow leaflets containing $2H_2O$, which is lost at 105°. The *nitrate* (cacothelin), obtained by heating brucine with 10 per cent. nitric acid at 60—70°, is an orange-coloured, crystalline powder, which becomes brown when exposed to light. The *hydrochloride* is crystalline, and dissolves in 45 parts of boiling water. M. O. F.

Ethylstrychnine and Benzylstrychnine. By NICOLA MOUFANG and JULIUS TAFEL (*Annalen*, 1898, **304**, 49—54. Compare Abstr., 1891, 1262).—The alkaline solutions obtained on treating strychnine ethiodide and benzylic chloride with moist silver oxide have been regarded by How and Garzarolli respectively as containing the corresponding ammonium bases ; the products are, however, ethylstrychnine and benzylstrychnine, arising from intramolecular rearrangement, thus,

$$OH \cdot NEt \vdots C_{20}H_{22}O \Big\langle \begin{matrix} CO \\ | \\ N \end{matrix} \quad \rightarrow \quad O \Big\langle \begin{matrix} NEt \\ -CO- \end{matrix} \Big\rangle C_{20}H_{22}O \vdots NH.$$

Ethylstrychnine (*strychnic acid ethylbetaine*), $O \Big\langle \begin{matrix} NEt \\ -CO- \end{matrix} \Big\rangle C_{20}H_{22}O \vdots NH,$

is prepared by gently heating strychnine ethiodide with silver sulphate and water, and boiling the filtrate with excess of barium hydroxide for a few minutes ; it crystallises from water in long, colourless needles containing $4H_2O$, and melts somewhat indefinitely at 260°. The behaviour of ethylstrychnine towards oxidising agents resembles that of the lower homologue.

Benzylstrychnine (*strychnic acid benzylbetaine*),

$$\begin{matrix} N(CH_2Ph) \\ O \text{——} CO \end{matrix} \Big\rangle C_{20}H_{22}O \vdots NH,$$
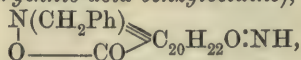
crystallises from hot water in colourless needles containing $9H_2O$; it melts at about 220°, and dissolves in about 10 parts of boiling water. Its behaviour towards oxidising agents resembles that of the foregoing substance. M. O. F.

Conversion-Temperature of Normal Strychnine Tartrate. By ALBERT LADENBURG and GUIDO DOCTOR (*Ber.*, 1899, **32**, 50—57. Compare Abstr., 1898, i, 707).—The sp. gr. of the three normal strychnic salts have been obtained by the aid of the pyknometer and benzene of sp. gr. = 0·86842 at 20°/4°, and equations for determining the rotatory power of solutions of different strengths have also been calculated.

		Sp. gr.	$[\alpha]_D \frac{20}{4}$.
1.	Racemate	1·36653	$-31·87924 + 3·7487\ p$.
2.	*l*-Tartrate	1·3405	$-31·36342 + 1·3564\ p$.
3.	*d*-Tartrate	1·43218	$-20·60725 + 0·9367\ p$.

p denotes the percentage of anhydrous salt in the solution, and the equation holds good for concentrations between $p = 0·5$ and $p = 2$ per cent. The rotatory power rapidly diminishes on dilution, especially in the case of the racemate. The rotation for the racemate agrees only with that for equal quantities of the *d*- and *l*-tartrates calculated from 2 and 3, between the concentrations $p = 1·82$ and

$p = 1.88$. The racemate is stable at the ordinary temperature, and at all temperatures below 30°.

Several of van't Hoff's methods have been adopted to determine the temperature at which the racemate becomes converted into the corresponding tartrates. The dilatometric method gave no definite results; a study of the solubility curves of mixtures of the tartrates and of the racemates indicated that at about 30° they crossed, and this would give the temperature of conversion at about 30°. Somewhat more correct results were obtained with the differential tensimeter, and the temperature was found to be 29·5°. It is pointed out that the usual conception, that a racemic acid, by the addition of an optically acid base, is directly resolved into salts of the two optically active acids, is erroneous. A partially racemic salt is first formed, and whether this or the salts of the two optically active acids crystallise out is merely a question of the temperature of conversion. J. J. S.

Alkaloid similar to Strychnine found in a Corpse. By Mecke and Wimmer (*Chem. Centr.*, 1898, ii, 111; from *Pharm. Zeit.*, **43**, 300—301).—The alkaloid which the authors have obtained from a corpse forms white, nodular crystals, and its hydrochloride, feathery, crystalline tufts. The alkaloid gives the same reactions as strychnine with picric acid, potassium dichromate and sulphuric acid, tannin, potassium ferricyanide, potassium thiocyanate, and nitric acid. The residue obtained after evaporating with chlorine water gives a dirty green coloration with ammonia. With Fröhde's reagent, the alkaloid gives first a dirty violet, then an olive, and, finally, a green coloration; with sulphuric acid, a yellow passing through cherry-red to rose-coloured, and with Erdmann's reagent, a yellow coloration. It has only a slightly bitter taste, and showed no physiological action on frogs. E. W. W.

Derivatives of Tropine. By A. F. P. van Son (*Chem. Centr.*, 1898, ii, 665—666 and 889—890; from *Ned. Tijdsch. Pharm.*, **10**, 242—257, 282. Compare Abstr., 1898, i, 282).—By the action of a solution of silver nitrate on tropine iodide hydriodide, $C_8H_{14}IN,HI$, in the cold, 1 atom of iodine is removed, but the second iodine atom is only attacked when the mixture is kept warm for a long time. According to the author, the hydriodide melts at 205—206° (Ladenburg 115°). *Tropine iodide hydrochloride*, $C_8H_{14}IN,HCl$, prepared by treating the hydriodide with moist silver chloride, crystallises from absolute alcohol in colourless plates and melts at 182°. The *aurichloride*, $C_8H_{14}IN,HAuCl_4$, forms yellow, star-shaped crystals, and melts at 167—168°; the *platinochloride*, $(C_8H_{14}IN)_2,H_2PtCl_6$, crystallises in brown, star-shaped prisms, and melts at 200°; the *mercurichloride*, $C_8H_{14}IN,HHgCl_3$, crystallises in long, branched needles and melts at 140—141°. *Tropine bromide hydrobromide* is prepared by heating tropine at 170—180° with 3—4 times its weight of hydrobromic acid solution saturated at 0°; it crystallises from alcohol in colourless, star-shaped crystals, melts at 216—217°, is easily soluble in water, slightly in alcohol, and insoluble in ether. The *hydrochloride of the bromide* crystallises in large, colourless prisms, melts at 204—205°, is easily soluble in water, and insoluble in ether; the

aurichloride crystallises in yellow needles, melts at 170°, and is easily soluble in water; the *platinochloride* crystallises in long, yellow needles, melts at 218—220°, and is easily soluble in water; the *mercurichloride* crystallises in white, feather-like crystals and melts at 165°. The author was unable to prepare tropine chloride corresponding with the above bromide and iodide, in a pure state, but analysis of its *aurichloride* indicated the composition $C_8H_{14}ClN,HAuCl_4$; it crystallises in yellow, feather-like crystals, and melts at 204—206°; the *platinochloride* melts at 226—227°. By the action of silver chloride in tropinethylene bromide, tropinecholine chloride is formed. Its *aurichloride* crystallises in lustrous plates and melts at 206—207°, and its *platinochloride* forms prismatic crystals and melts at 217°; both compounds are anhydrous.   E. W. W.

Datura Alba and Hyoscine. By OSWALD HESSE (*Annalen*, 1898, **303**, 149—165).—The presence of hyoscine in the blossoms of the Chinese *Datura alba* has been observed by Browne, who ascribed to the alkaloid the empirical formula given by Ladenburg, namely, $C_{17}H_{23}NO_3$. The author, having previously shown that the composition is probably $C_{17}H_{21}NO_4$, has examined the alkaloid from the source indicated, and considers that the result confirms his original view.

Hyoscine is amorphous, and dissolves very readily in cold water; potassium hydrogen carbonate precipitates it unchanged from solutions of the hydrobromide. Under conditions described in the paper, hyoscine is not converted into atroscine by the agency of silver oxide or caustic soda.   M. O. F.

Laurotetanine: the Alkaloid of the Bark of Tetranthera Citrata. By J. D. FILIPPO (*Arch. Pharm.*, 1898, **236**, 601—622). —Laurotetanine, $C_{19}H_{23}NO_5$, was extracted from the bark of *Tetranthera citrata* (*Litsaea citrata*) by Greshoff's method, 20 kilograms of the bark yielding 50 grams of the alkaloid. It crystallises from ether in almost colourless groups of needles, melts at 134°, has a bitter, somewhat burning, taste, and is almost insoluble in water, ether, and benzene, but readily soluble in alcohol, chloroform, acetone, and ethylic acetate. Its alcoholic solution has an alkaline reaction. It gives characteristic colour reactions with concentrated nitric and sulphuric acids, is easily decomposed, and is especially characterised by its strongly reducing properties. The *aurichloride* is an unstable, amorphous, yellow precipitate; the *platinochloride* forms small, reddish-yellow crystals; the *hydrochloride,* $C_{19}H_{23}NO_5,HCl + 6H_2O$, crystallises in thick needles melting at 46°, the dried substance decomposes without melting at 230°; the *hydrobromide,* $C_{19}H_{23}NO_5,HBr + 2H_2O$, forms colourless needles; the *hydriodide,* $C_{19}H_{23}NO_5,HI + 2H_2O$, crystallises in groups of pale yellow needles; the *sulphate,* $(C_{19}H_{23}NO_5)_2,H_2SO_4 + 5H_2O$, forms small, prismatic crystals, and the *picrate* crystallises in small, yellow needles decomposing at 150°, without melting.

When heated with methylic iodide, the alkaloid is converted into the hydriodide, but with ethylic iodide, *ethyl-laurotetanine hydriodide,* $C_{19}H_{22}EtNO_5,HI$, is formed, crystallising from water in small needles melting at 212°, and proving that the alkaloid is a secondary base.

By the action of sodium carbonate on the hydriodide, *ethyl-laurotetanine* is obtained, crystallising from glacial acetic acid in small needles melting at 127—130°. It has a strong reducing reaction, but owing to scarcity of material its properties could not be thoroughly investigated.

Laurotetaninephenylthiocarbamide, $NHPh \cdot CS \cdot NC_{19}H_{22}NO_5$, prepared by the action of phenylthiocarbimide on the alcoholic solution of the base, crystallises from alcohol in needles melting at 211—212°. Ethyl-laurotetanine is not acted on by phenylthiocarbimide.

Hydroxylamine and phenylhydrazine are without action on the alkaloid, which was shown to contain three methoxy-groups. By the action of benzoic chloride, a crystalline substance is obtained melting at 194°, and is probably a *dibenzoyl* derivative, although this has not so far been definitely proved.

From experiments made on frogs, the alkaloid acts as a cramping poison, producing reflex action of the central nerve system.

A. W. C.

Diastase. By WALTER J. SYKES and H. NEVILLE HUSSEY (*J. Fed. Inst. Brew.*, 1898, **4**, 527—544).—In order to avoid the employment of alcohol in the preparation of diastase from malt, the authors used saturated solutions of sodium sulphate and magnesium sulphate ; the precipitates, however, obtained in this way were found not to be very active. From barley, an active diastase was obtained by precipitation with a saturated solution of ammonium sulphate. Experiments made with the object of splitting up diastase by means of fractional precipitation with ammonium sulphate gave negative results. The precipitate given by magnesium sulphate was found to be capable of inverting cane-sugar, showing that some, at least, of the invertase of the malt is thrown down with the diastase. A. C. C.

Presence of a Soluble Proteolytic Ferment in Certain Fungi. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1898, **127**, 666—669).—It has appeared from previous researches that the only fungus capable of producing a proteolytic enzyme is *Aspergillus niger*, an aqueous maceration of which acts on fibrin and albumin in the same manner as an aqueous solution of trypsin. It is now shown, however, that twenty out of twenty-six fungi examined, when macerated with sand and water containing chloroform, yield a solution which, after filtration, is capable of almost completely digesting casein, yielding peptones together with tyrosine. The above-mentioned fungi are thus capable of elaborating an enzyme analogous to, if not identical with, trypsin ; it is destroyed when its solution is boiled, although not affected by the presence of chloroform. The casein employed was in the form of milk from which the fats had been removed by means of alcohol-ether containing ammonia ; the ferment thus acted in presence of small quantities of alcohol and ammonia.

W. A. D.

Laccase : A New Oxidising Soluble Ferment. By GABRIEL BERTRAND (*Ann. Chim. Phys.*, 1897, [vii], **12**, 115—140).—This paper refers to work already published (compare Abstr., 1895, i, 386 ; 1896, i, 534, ii, 61, 571 ; 1897, ii, 117 ; 1898, i, 53, ii, 128).

G. T. M.

Oxydases and the Guaiacum-Reaction. By J. Grüss (*Chem. Centr.*, 1898, ii, 366; from *Ber. Deutsch. bot. Ges.*, 16, 129—139).—The author distinguishes three oxydases and describes their distribution in plants. *a-Oxydase* is soluble in glycerol and is partially precipitated from its solution by lead acetate without decomposing. *β-Oxydase* is also soluble in glycerol and is precipitated by alcohol and ether; it can be detected in potatoes by leaving the resting tubers in alcohol for several days, or by heating them with alcohol at 50—53° for 10 minutes. *γ-Oxydase* is not decomposed even by boiling alcohol, and is detected by the blue coloration obtained with guaiacum-hydrogen peroxide after boiling the specimen to be tested with alcohol for ¼—1 hour.   E. W. W.

Colouring Matter of Bile. By William Küster (*Zeit. physiol. Chem.*, 1898, 26, 314—337. Compare Abstr., 1897, i, 647).—The author has repeated his previous experiments with larger quantities of materials, and gives a detailed account of the preparation of crystallised bilirubin, $C_{16}H_{18}N_2O_3$, and its subsequent oxidation into biliverdin, $C_{16}H_{18}N_2O_4$. A yield of 20 per cent. of biliverdic acid, $C_8H_9NO_4$, is obtained when biliverdin is oxidised with a hot acetic acid solution of sodium dichromate. The *silver*, *calcium*, and *ammonium* salts of this acid all contain $1H_2O$; the basic *cadmium* salt crystallises in aggregates of needles. When titrated with cold alkali, biliverdic acid is monobasic, but slowly changes into a dibasic compound, and on boiling with caustic soda it evolves ammonia and becomes converted into the lactone of tribasic hæmatic acid, $C_8H_8O_5$. This hydrolysis indicates the close relationship existing between the blood and bile-colouring matters; the molecules of bilirubin and hæmatin both contain complexes from which the substance $C_8H_8O_5$ can be obtained, although the yield from biliverdin is only half that from hæmatin.
                                    G. T. M.

Bromo-proteinchrome. By D. Kuraéeff (*Zeit. physiol. Chem.*, 1899, 26, 501—512).—Among the products of digestive proteolysis, the one which gives a colour with bromine has hitherto been little investigated chemically. Under some circumstances, a red, under others a black, under others, again, a bluish-violet product is obtained. The osmotic properties of these substances are on about the same level as those of peptone. Elementary analyses are given, and the substances contain carbon, hydrogen, bromine, nitrogen, sulphur, and oxygen, the percentage of bromine varying from 24 to 34. The coloured products are believed to be bromine derivatives of albumoses.   W. D. H.

Union of Iodine with Crystallised Egg-albumin and Serum-albumin. By D. Kuraéeff (*Zeit. physiol. Chem.*, 1899, 26, 462—486). —Crystalline albumin was prepared according to the recognised methods, but without the addition of acid. Iodine was added in a potassium iodide solution, or as a mixture of iodide and iodate of potassium, the precipitate being dissolved in weak ammonia and again precipitated by acids. Its properties were like those of Hofmeister's iodalbumin; the percentage of iodine in the serum-albumin preparation varied from 9·86 to 12·28, the average in ten

preparations being nearly 12. From the analyses, the empirical formula, $C_{450}H_{693}I_{11}N_{116}S_4O_{132}$, may be deduced. The percentage of iodine in the preparation from egg-albumin is less.　　　　W. H. D.

Decomposition of Albumin by Hydrochloric Acid. II. By RUDOLF COHN (*Zeit. physiol. Chem.*, 1899, **26**, 395—410. Compare Abstr., 1896, i, 658; 1898, i, 343).—In previous work, the author succeeded in obtaining products which accounted for 91 per cent. of the casein originally taken, and by more careful analysis he has now brought this number up to 97·8; of this, tyrosine accounts for 3·5 and leucine for 31 per cent. Glutamic acid is a large constituent of the products obtained, whilst pyridine derivatives are only present in small quantity.

Benzoic chloride is a good precipitant for lysine.

Horny material was subjected to similar treatment; the most striking point in the results is the high percentage of tyrosine obtained.　　　　　　　　　　　　　　　　　W. D. H.

Oxidation of Albumin with Permanganate. By RICHARD BERNERT (*Zeit. physiol. Chem.*, 1898, **26**, 272—307. Compare Maly, Abstr., 1885, 824; 1888, 1120; and 1889, 629).—When oxyprotosulphonic acid, obtained from egg-albumin by oxidation with potassium permanganate, is subjected to Pick's method of fractional precipitation with ammonium sulphate (Abstr., 1898, i, 288 and 608), it is separated into two fractions, whereas that obtained from crystallised serum-albumin appears to be homogeneous. Leucine and aspartic and melanoidic acids are obtained on hydrolysing oxyprotosulphonic acid with concentrated hydrochloric acid, but tyrosine and glutamic acid cannot be detected among the products of reaction. If, as Maly assumed, the oxidation of albumin to oxyprotosulphonic acid is effected without fission of the molecule, this action should not be attended by the formation of bye-products; it is found, however, that considerable quantities of substances resulting from the decomposition of albumin are simultaneously produced, and the author suggests that oxyprotosulphonic acid may differ considerably in molecular complexity from the parent substance, and that the hydrolytic action of the alkali set free during oxidation must also be taken into account. The mother liquors from the oxyprotosulphonic acid are neutralised with ammonia and concentrated until potassium sulphate separates; the filtrate, when treated with ammonium sulphate, yields a precipitate which is redissolved in water and fractionated by means of the same reagent into three albumoses. From the final mother liquors, two peptones are obtained, which differ in their solubility in alcohol. A table is given showing the behaviour of these albumoses and peptones towards the usual reagents for proteid substances. Like oxyprotosulphonic acid, these five substances yield neither scatole nor indole on fusion with potash, they contain no loosely combined sulphur as indicated by the lead acetate test, and they give negative results with Millon's, Adamkiewicz's, and the xanthoproteic reactions. The fatty acids present in the mother liquors, after precipitating the albumoses, are separated by distillation with steam and converted into their ethylic salts; acetic and propionic acids are thus identified, whilst the amount of butyric

acid obtained is so small that it is impossible to determine whether it is the normal or iso-compound. The bases, obtained by precipitation with phosphotungstic acid, are histidine and arginine, together with a compound probably identical with lysine. The author finds that Maly's peroxyprotoic acid, produced by the oxidation of oxyproto-sulphonic acid, is not homogeneous, but consists of two substances giving different figures on analysis ; one of these is precipitated by mercuric acetate, and yields leucine, pyridine, acetic and butyric acids, but no trace of pyrroline or glutamic acid on hydrolysis with barium hydroxide, the other substance is precipitated by lead acetate, and when hydrolysed gives leucine, benzaldehyde, benzoic, acetic, propionic, and butyric acids ; neither amidovaleric nor isoglyceric acids, obtained by Maly under these conditions, could be detected among the products.

G. T. M.

The Albumoses of Witte's Peptone. By HUGO SCHRÖTTER (*Zeit. physiol. Chem.*, 1898, **26**, 338—342).—The author refers to his previous work on the subject (Abstr., 1894, i, 215 ; 1896, i, 112, 515 ; 1898, i, 610), and complains of the scant notice it has received in recent publications by others. W. D. H.

Organic Chemistry.

Solubility of Organic Compounds in Water. By WILHELM VAUBEL (*J. pr. Chem.*, 1899, [ii], **59**, 30—45).—The solubility of gaseous aliphatic compounds in water is greatest when a triple bond is present and least when only single bonds occur; as a rule, it decreases with increase of the percentage of carbon. As regards liquid and solid compounds, both aliphatic and aromatic, it is only the oxygen derivatives which are appreciably soluble in water, and their solubility is less the greater the percentage of carbon. In the case of the monhydric alcohols and monobasic acids, solubility practically ceases when 5 or 6 atoms of carbon are present, a number which may be conceived as arranged in a ring without too great a displacement from their normal positions. Incidentally, it was found that aqueous solutions of aldehyde have a maximum density corresponding with about 20 per cent. of aldehyde. In the oxalic acid series, the solubility alternately rises and falls, as does the melting point; it is large when an odd number of carbon atoms is present, comparatively small when the number is even. The author seeks to explain this by means of his space formulæ (compare Abstr., 1898, i, 129); it is to the presence of the COOH groups that the solubility must be attributed, and in the acids with an even number of carbon atoms these groups lie towards opposite sides of the molecule, and so tend to neutralise each other, whilst they lie towards the same side, and, therefore, reinforce each other, when the number of carbon atoms is odd. In harmony with this view is the fact that fumaric acid is but slightly soluble in water, whilst maleic acid is very soluble. In a similar fashion, it is sought to explain the smaller solubility of paradihydroxybenzene, diamidobenzene, and benzenedicarboxylic acid, as compared with the meta-isomerides; further, ortho-derivatives are compared with acetylenedicarboxylic acid. The influence of the nature and position of the substituting groups on the specific volume of the solution is also considered in a few cases.

C. F. B.

Action of Magnesium on Nitrogenous Compounds, especially Cyanides. By W. EIDMANN (*J. pr. Chem.*, 1899, [ii], **59**, 1—22).— When silicon nitride is heated with excess of magnesium powder in the absence of air, magnesium nitride and silicon, or magnesium silicide, are formed, as the residue yields ammonia when treated with water, and hydrogen and silicon hydride when treated with hydrochloric acid. With boron nitride, analogous results are obtained. With cyanogen, with hydrogen, methylic, ethylic, and phenylic cyanides, and with aniline, acetanilide, nitrobenzene, pyridine, quinoline, and carbazole, magnesium nitride and carbon are obtained, magnesium carbide also being produced in the case of compounds containing a cyanogen group.

The action on metallic cyanides was studied in greater detail in the case of barium cyanide. Coarse magnesium powder (about 3 at.) was mixed with this substance (1 mol.), the mixture placed in a nickel crucible, of which it occupied about one-third, covered with

asbestos paper, then with a thick layer of asbestos, and last of all with sand; the mixture was then heated with a small flame until a reaction occurred. The product yielded ammonia and acetylene when treated with water, and when crystallised barium cyanide had been used, a little hydrogen also; the aqueous solution contained barium hydroxide and undecomposed barium cyanide, and the residue consisted of magnesium hydroxide and unaltered magnesium. The original product must, therefore, have contained magnesium nitride, barium carbide, and barium; the last substance could, indeed, be separated by digesting the mass with mercury and pressing the amalgam formed through leather. Estimations of the amounts of ammonia and acetylene formed, showed that magnesium nitride is always produced in almost theoretical quantity, whilst the yield of carbide is below the theoretical, becoming less the higher the temperature to which the mixture is heated. This is explained by supposing that the main reaction takes place thus: $Ba(CN)_2 + 3Mg = BaC_2 + Mg_3N_2$; but that at the high temperature produced, some of the barium cyanide is decomposed thus: $Ba(CN)_2 = Ba + C_2N_2$, the cyanogen being decomposed by the magnesium, $C_2N_2 + 3Mg = Mg_3N_2 + 2C$, so that the yield of cyanide is maintained at the theoretical. Variation of the proportion between the barium cyanide and the magnesium hardly seemed to influence the course of the reaction.

The action of magnesium on the cyanides examined is thus summarised. The reaction is more violent the more easily the cyanide is decomposed by heat; in addition to this decomposition, the reaction indicated in the first equation given above occurs to some extent, but if the carbide formed is easily decomposed by heat, as is the case with the carbides of the alkali metals and magnesium, it yields metal and carbon, $M''C_2 = M'' + 2C$. "The cyanides fall into three groups, as regards the action of magnesium on them. (1) Those which are stable at a red heat, $Ba(CN)_2$, $Ca(CN)_2$, $Sr(CN)_2$, $Mg(CN)_2$, KCN, and NaCN, react as soon as a red heat is reached and with no, or but a very mild, explosion, the temperature rising to a bright red heat. The product consists chiefly of magnesium nitride and metallic carbide. (2) Those cyanides which decompose at a red heat, $Zn(CN)_2$, $Cd(CN)_2$, $Ni(CN)_2$, $Co(CN)_2$, $Pb(CN)_2$, and $Cu_2(CN)_2$, are decomposed, with the production of a bright red heat and a feeble explosion. The residue consists chiefly of magnesium nitride, metal, and carbon. (3) Those cyanides which decompose below a red heat, AgCN and $Hg(CN)_2$, first decompose, for the most part, into metal and cyanogen, on the latter of which the magnesium then acts with a violent explosion, a red heat being produced. The residue contains metal, carbon, and magnesium nitride, the last two of which must be regarded as resulting from the action of the magnesium on the cyanogen liberated."

C. F. B.

Cyanide of Mercury. By L. PRUSSIA (*Gazzetta*, 1898, **28**, ii, 113—122).—Mercuric cyanide readily combines with other compounds of mercury, forming double salts.

A compound, $HgCl_2,HgCy_2$, is formed on dissolving the constituent salts in a small volume of water at 40—50°; the liquid deposits

microscopic octahedra and prisms, apparently dimetric, which are very soluble in water, and slightly so in boiling alcohol.

The compound $HgBr_2,HgCy_2$ is produced on extracting with boiling alcohol an intimate mixture of mercuric bromide and cyanide in molecular proportion, and by slow evaporation of the solution is obtained in colourless, transparent prisms, which are very slightly soluble even in boiling water, and remain unchanged on exposure to the air.

The compound $Hg(NO_3)_2,HgCy_2$ is formed when the constituent salts are ground up with a little water; it is a white, crystalline powder, very soluble in water, from which it crystallises in rhombic laminæ. It readily decomposes on heating, even its hot aqueous solution evolving carbonic anhydride and depositing metallic mercury. Ethylic alcohol seems to decompose it, but a methylic alcohol solution is not affected even on boiling. Potassium hydroxide or sodium carbonate decomposes the aqueous solution.

By triturating together mercuric cyanide and acetate, a limpid liquid is obtained, which, after a short time, deposits a double salt of the composition $Hg(C_2H_3O_2)_2,HgCy_2$ in transparent, colourless prisms very soluble in water or alcohol. On adding caustic soda to its aqueous solution, crystalline mercuric oxycyanide is precipitated.

Mercuric cyanide differs in behaviour from most other metallic salts, as, for instance, in its stability towards alkali hydroxides; this points to the fact that its aqueous solution does not contain the ion Hg. Cryoscopic determinations in aqueous solutions show further that mercuric cyanide is not an electrolyte.

On adding caustic alkali to mercuric cyanide, slight decomposition sometimes occurs, so that on the addition of ferroso-ferric sulphate and a dilute acid, Prussian blue is precipitated; this is due, the author points out, to the presence in the alkali of small quantities of halogen salts which react with the mercuric cyanide, giving alkali cyanide and mercuric haloid.

The use of Plugge's reaction, namely, the evolution of hydrogen cyanide when mercuric cyanide is treated with common salt and oxalic acid, has been suggested for the toxicological estimation of mercuric cyanide. The author has devised an improved method of carrying out this process; he substitutes tartaric for oxalic acid, and uses a stream of carbonic anhydride to expel the hydrogen cyanide, which is absorbed by slightly ammoniacal silver nitrate: the addition of an acid to the solution precipitates silver cyanide, which can be weighed. By employing potassium bromide or iodide in place of common salt, the reaction is accelerated, and more accurate results are obtained.

T. H. P.

Chromium Tetroxide Potassium Cyanide. By O. Fritz Wiede (*Ber.*, 1899, **32**, 378—387).—When the compound $CrO_4,3NH_3$, prepared by the action of strong ammonia on perchromic acid (Abstr., 1898, ii, 20), is treated with an aqueous solution of potassium cyanide, it dissolves with an intense, brownish-red coloration, ammonia being at the same time eliminated, and on adding alcohol, a brownish-red oil separates which solidifies in large crystals after some time.

Chromium tetroxide potassium cyanide, $CrO_4,3KCN$, is readily soluble in water but insoluble in all other solvents; the brownish-red, aqueous solution gradually decomposes with elimination of hydrogen cyanide and formation of the chromate. Many salts produce characteristic precipitates; with dilute sulphuric acid, on warming, it is decomposed into hydrogen, oxygen, and chromic sulphate, but in the cold only a change of colour from brownish-red to violet occurs; this colouring matter may be extracted by means of ether, and is evidently due to chromium tetroxide hydrogen cyanide, which, however, cannot be isolated, the ethereal solution, on evaporation, yielding only chromate and hydrogen cyanide.

The potassium cyanide compound cannot be formed directly by adding an aqueous solution of potassium cyanide in alcohol to an ethereal solution of perchromic acid, as under these conditions a dark violet liquid separates, which when left solidifies, forming black crystals of the compound $KCrO_5 + H_2O_2$; this is identical with the potassium salt of perchromic acid, previously described, but being in a much purer form has not only a darker colour, but is also crystalline and non-explosive; it cannot be obtained without hydrogen peroxide of crystallisation.

The paper concludes with measurements of the crystals both of chromium tetroxide ammonia and of chromium tetroxide potassium cyanide. J. F. T.

Barium Platinocyanide and Platinum free from Iridium. By PAUL BERGSÖE (*Zeit. anorg. Chem.*, 1899, **19**, 318—326).—Barium platinocyanide is best prepared by adding to a solution of hydrogen platinochloride the theoretical quantity of barium hydroxide and hydrogen cyanide, and treating the warm mixture with sulphurous anhydride until it becomes colourless; after removing the precipitated barium sulphate by filtration, the barium platinocyanide crystallises completely from the solution, as it is almost insoluble in a cold solution of barium chloride. The reaction which takes place in the preceding method is expressed by the equation $H_2PtCl_6 + 4HCN + 5Ba(OH)_2 + SO_2 = BaPt(CN)_4 + 3BaCl_2 + BaSO_4 + 8H_2O$.

The formation of barium platinocyanide proved to be a very convenient method for the preparation of platinum free from iridium, as this salt is easily purified by crystallisation from water, being soluble in 3—4 parts of boiling water and in 30 parts of cold water. Forty grams of platinum containing traces of iridium were mixed with a further 0·25 gram of iridium and converted into the barium double cyanide as described above. The barium platinocyanide was re-crystallised three times from water, and the mother liquors evaporated to about one-third or one-fourth their volume, the further separations being mixed with the main product. The yield obtained was 30 grams, or 75 per cent., of platinum free from iridium; the barium sulphate precipitate contained 2·45 grams of platinum and 0·05 gram of iridium; the mother liquors contained 7·015 grams of platinum and 0·281 gram of iridium. This method gives a much better yield than that based on the purification by means of sodium platinochloride. Traces of osmium, ruthenium, and rhodium are completely removed with the iridium, but palladium, which forms a double cyanide isomorphous with

that of platinum, cannot be removed by this method ; fortunately, however, it is easily and completely removed by the ordinary methods of purification.

The estimation of iridium in platinum when the iridium is present to the extent of 0·1 per cent. or above, is very quickly effected by comparing the colour of the precipitate obtained by adding potassium chloride with that of the precipitate obtained from a sample containing a known quantity of iridium. It is, however, necessary that both precipitates should be formed under precisely the same conditions as regards concentration, temperature, and the quantity of potassium chloride solution. When less than 0·1 per cent. of iridium is present, it is estimated according to the method described by Deville and Stas. The sample is heated with pure lead at 1000° for about five hours in a porcelain crucible in a current of coal gas ; the lead alloy is treated with nitric acid, and the insoluble residue extracted with aqua regia, whereby the platinum is dissolved and the iridium and ruthenium remain insoluble. To remove any silicates which may be formed by action on the porcelain crucible, the residue of iridium is washed with hydrofluoric acid and finally ignited, reduced in a current of coal gas, and weighed.　　　　　　E. C. R.

Double Thiocyanates of Vanadium and the Alkalis. By A. Cioci (*Zeit. anorg. Chem.*, 1899, **19**, 308—317).—*Potassium vanadium thiocyanate*, $V(SCN)_3,3KSCN + 4H_2O$, is obtained by dissolving vanadic anhydride in sulphuric acid, treating the solution with sulphurous anhydride, and after driving off the excess of the gas by heating on the water-bath, reducing the solution with the electric current until it becomes green. The green solution is then precipitated with potassium hydroxide, the theoretical quantity of potassium thiocyanate added, and the solution evaporated on the water-bath ; the product is then extracted with 95 per cent. alcohol in order to remove the potassium sulphate, and the solution evaporated to dryness. This operation is twice repeated, and, finally, the salt is crystallised from water ; it forms bright red crystals, which gradually become anhydrous when allowed to remain in a vacuum over sulphuric acid, or when heated at 100°, decomposes at 110°, and on further heating yields a black mass of partially reduced vanadic acid. It is easily soluble in water and alcohol, sparingly so in ether. The aqueous solution gives a precipitate of vanadium hydroxide when treated with alkalis or with ammonium sulphide. It is not precipitated by salts of magnesium, zinc, cadmium, manganese, cobalt, or nickel, but with copper sulphate it gives a black precipitate, and with mercurous nitrate a grey precipitate ; both precipitates turn white after a time. With silver nitrate, it yields a reddish-brown precipitate which changes to violet and grey, and is blackened when treated with ammonia. Both the chemical reactions and the results obtained by the cryoscopic determination of the molecular weight show that the substance is a double salt, whereas potassium chromium thiocyanate is the salt of a complex acid.

Ammonium vanadium thiocyanate, $V(SCN)_3,3NH_4SCN + 4H_2O$, separates in dark green to black crystals, and closely resembles the potassium salt.

Sodium vanadium thiocyanate, $V(SCN)_3,3NaSCN + 12H_2O$, crystallises in large, red tablets or leaflets, is extremely hygroscopic, melts in its water of crystallisation at 68°, and is similar in other respects to the preceding salts.

Sodium chromocyanate has been described by Roesler as crystallising with $7H_2O$; the author has prepared it according to Roesler's method, and finds that it crystallises with $12H_2O$. All the vanadium thiocyanate salts, therefore, have a composition analogous to that of the chromium salts.

The author was unable to obtain nickel and barium double salts of vanadium thiocyanate. E. C. R.

Nitro-alcohols. By JOSEPH MAAS (*Rec. Trav. Chim.*, 1898, **17**, 384—398).—*ββ-Bromonitroethylic alcohol*, $NO_2 \cdot CHBr \cdot CH_2 \cdot OH$, prepared by the condensation of bromonitromethane with formaldehyde under the influence of a little potassium carbonate, is a thick, yellowish liquid having a pungent odour, boils at 147—148° under 45 mm. pressure, and is sparingly soluble in water, but dissolves in ether and alcohol. Its molecular weight in water is normal; its sp. gr. is 2·084 at 10°, and its refractive index at ordinary temperature is 1·52952. The *nitrate* is a somewhat viscid, yellowish liquid of sp. gr. = 2·438 at 11°. The *acetate* is a colourless liquid of sp. gr. = 1·958 at 11°, and boils at 138—142° under 50 mm. pressure.

When bromonitroethylic alcohol is heated with water at 135—140°, the liquid is found to have strong reducing properties, and yields a crystalline sodium salt on neutralisation and agitation with sodium hydrogen sulphite.

ββ-Bromonitrotrimethylenic glycol, $NO_2 \cdot CBr(CH_2 \cdot OH)_2$, obtained by the action of formaldehyde (2 mols.) on bromonitromethane (1 mol.) or bromonitroethylic alcohol (2 mols.) in presence of potassium carbonate, forms beautiful, colourless, transparent crystals, which are more or less octahedral in form; it melts at 106—107°, is sparingly soluble in water, but dissolves in alcohol and ether, and has the normal molecular weight in water.

ββ-Bromonitroisopropylic alcohol, $NO_2 \cdot CHBr \cdot CHMe \cdot OH$, obtained from bromonitromethane and acetaldehyde, is a colourless liquid, but becomes yellow on exposure to light, has a faint but acid odour and a pungent taste; it has a sp. gr. = 1·899 at 10°, boils at 149—150° under 42 mm. pressure, and has the normal molecular weight in cold water, in which it is almost insoluble, but dissolves in alcohol and ether. The *nitrate* is a colourless, oily liquid insoluble in water, and has a sp. gr. = 2·134 at 10°. The *acetate* is a colourless, oily liquid having a faint odour of acetic acid, has a sp. gr. = 1·820 at 11°, and boils at 139—141° under 48 mm. pressure.

ββ-Bromonitrobutylenic αγ-glycol, $OH \cdot CHMe \cdot CBr(NO_2) \cdot CH_2 \cdot OH$, is the product of interaction of acetaldehyde and bromonitroethylic alcohol or of formaldehyde and bromonitropropylic alcohol. It forms beautiful, transparent, colourless crystals, is insoluble in water, and melts at 94—96°.

Bromonitromethane condenses with piperidylcarbinol, yielding a colourless, crystalline *substance* melting at 49—51°, which rapidly

undergoes alteration and becomes brown; it was not obtained in condition suitable for analysis.   A. L.

Acetonechloroform. By FRANK K. CAMERON and H. A. HOLLY (*Journ. Physical Chem.*, 1898, **2**, 322—335. Compare Willgerodt, Abstr., 1882, 492; 1883, 1079; 1885, 648; 1888, 810; 1889, 689; 1890, 959).—The authors have repeated the greater part of Willgerodt's work, and come to the conclusion that there is but one acetonechloroform, a white, crystalline solid, which is trichlorotrimethylcarbinol, $CCl_3 \cdot CMe_2 \cdot OH$. This substance is not a simple additive product, and cannot be resolved into its original constituents by any direct means. It forms no definite hydrate. The temperature of the quadruple point for solid, two solutions and vapour, in the system acetonechloroform | water is 75·2°. Its melting point is near, but above 97°, and in all probability a perfectly anhydrous substance has not yet been obtained. The system acetonechloroform and water seems to present the remarkable case of a solid solution and two liquid solutions.   J. J. S.

Action of Zinc Chloride on Amylic Alcohol. By J. WALTHER (*J. pr. Chem.*, 1899, [ii], **59**, 41—45).—This reaction may be supposed to take place in two stages, like that of sulphuric acid on alcohol; the first stage would be expressed by the equation, $C_5H_{11} \cdot OH + ZnCl_2 = C_5H_{11} \cdot O \cdot ZnCl + HCl$. To test this supposition, anhydrous amylic alcohol (1 mol.) was warmed with dry zinc chloride (1 mol.) until amylene began to come off; the zinc chloride dissolved gradually, and at 40° an evolution of gas commenced. The mixture was cooled and extracted with ether; by adding light petroleum to the ethereal extract, a compound was precipitated, and this was purified by repeated solution in ether and precipitation with light petroleum. It forms a yellowish-red syrup, and yields amylic alcohol and zinc oxychloride when treated with water; and small quantities of amylic alcohol, amylene, diamylene, and aldehyde, together with a pasty residue left in the flask, when it is distilled under either ordinary or diminished pressure.   C. F. B.

Synthesis of Dimethylheptenol. By PHILIPPE BARBIER (*Compt. rend.*, 1899, **128**, 110—111).—The synthesis of 2 : 6-dimethyl-2-heptene-6-ol has been effected by the general method devised by Saytzeff, in which, however, magnesium was used instead of zinc, a modification which was found to be of considerable service in this and other syntheses. Methylic iodide (113 grams) is gradually added to a well-cooled mixture of natural methylheptenone (100 grams) with anhydrous ether (150 grams) and magnesium turnings (20 grams); the magnesium compound formed is decomposed by dilute sulphuric acid, and the liquid which separates is purified by fractional distillation under diminished pressure. The dimethylheptenol which is thus obtained is a colourless liquid boiling at 79—80°, and is identical in every respect with the product of the action of alcoholic potash on lemonol.   N. L.

Biochemical Oxidation of Propylenic Glycol. By ANDRÉ KLING (*Compt. rend.*, 1899, **128**, 244—246).—When propylenic glycol

is mixed with an infusion of beer yeast, sterilised, inoculated with a culture of the sorbose bacterium and kept at 30°, it is partially converted into pyruvic aldehyde or into the acetol, $CH_3 \cdot CO \cdot CH_2 \cdot OH$, described by Perkin, probably the latter, but the point was not definitely determined.

Purification of propylenic glycol by distillation is unsatisfactory, since increasing quantities of aldehydes are formed, and they exert an antiseptic action in experiments with organisms. The best results are obtained by mixing the commercial "pure" propylenic glycol with its own volume of water, agitating five or six times with small quantities of ether, and then allowing the aqueous solution to evaporate over calcium chloride; the residual glycol is quite free from aldehydes.

<div align="right">C. H. B.</div>

Action of Liquid Hydrogen Iodide on Ether. By F. G. COTTRELL and ROY RAVONE ROGERS (*Amer. Chem. J.*, 1899, **21**, 64—66. Compare Abstr., 1896, ii, 357).—A vigorous action occurs when ether is mixed with an excess of liquid hydrogen iodide; the product, after remaining for a week, consists of ethylic iodide and water, the amount of the former substance produced is 94 per cent. of the theoretical ($Et_2O : 2EtI$).

<div align="right">G. T. M.</div>

d- and *r*-Arabinose. By OTTO RUFF (*Ber.*, 1899, **32**, 550—560).— By employing hydrogen peroxide and basic ferric acetate as an oxidising agent, a 25 per cent. yield of pure *d*-arabinose may be obtained from calcium *d*-gluconate.

d-Arabinose and *l*-arabinose both melt at 158·5—159·5 (corr.) when recrystallised from alcohol; *r*-arabinose melts at 163·5—164·5° (corr.), and is much more soluble than either of its active constituents; its true racemic nature is further shown by a determination of its molecular weight by the freezing point method. *d*-Arabitol, formed by the reduction of *d*-arabinose, melts at 103° (corr.), and *r*-arabitol at 105—106° (corr.); *d*-arabonic acid, prepared by the oxidation of *d*-arabinose with nitric acid, is a colourless syrup which, on heating, passes into the *lactone*; this crystallises from acetone in colourless needles melting at 98—99° (corr.). Calcium *d*-arabonate is identical in form with the *l*-modification, but a mixture of the two does not form a true racemic compound, but merely is a mixture of the two active constituents. *r*-*Arabonic lactone* crystallises from acetone in large, prismatic needles melting at 115—116° (corr.), and is less soluble in acetone than its active isomerides. *d*-*Trihydroxyglutaric acid* crystallises from acetone in hexagonal prisms melting at 128° (corr.). *r*-*Trihydroxyglutaric acid* melts at 154·5° (corr.), and is very similar in its properties to Fischer's *i*-xylotrihydroxyglutaric acid. The affinity constant of *l*-trihydroxyglutaric acid is nearly twice as great as that of the *r*-acid, the former being 0·132, and the latter 0·069.

<div align="right">J. F. T.</div>

Properties of Soluble Starch, and a Simple Method for its Preparation. By AUGUSTIN WRÓBLEWSKI (*Chem. Zeit.*, 1898, **22**, 375—376).—Soluble starch is the first product formed in the hydrolysis of starch; it is characterised by its solubility, by passing through

a porcelain filter, by not reducing Fehling's solution, and by giving a blue coloration with iodine. The author thinks it may also be regarded as the highest dextrin, although it differs in several of its properties from the ordinary dextrins (compare Lintner, Abstr., 1898, i, 460). For the preparation of soluble starch, the following method is recommended. Hoffmann's rice starch (20 grams) is rubbed in a mortar with cold water (100 c.c.) poured into a 2-litre flask, boiling 0·5 per cent. aqueous potassium hydroxide (1 litre) is added, and the mixture well shaken; after being boiled for 1·5—2 hours, the solution is filtered, neutralised with dilute acetic acid, and the soluble starch precipitated with 95 per cent. alcohol. The precipitate is filtered, washed with 50 per cent., with 95 per cent., and with absolute alcohol, then with ether, and finally dried in a vacuum. The amount of alcohol required to precipitate soluble starch from aqueous solutions depends on the amounts of salts present, and if these are not present, it is advisable to add small quantities of neutral salts, such as potassium acetate.

It is thought that Syniewski's product, obtained by the action of sodium peroxide on starch, is not soluble starch, but a product of oxidation (Abstr., 1898, i, 61). J. J. S.

γ-**Amido-$\alpha\beta$-propylenic Glycol.** By K. CHIARI (*Monatsh.*, 1898, **19**, 571—583).—*Acetoallylamide*, CH_2:$CH\cdot CH_2\cdot NHAc$, is obtained on adding excess of acetic anhydride gradually to well-cooled allylamine, heating on the water-bath, and finally distilling off the excess of acetic anhydride. It is a fairly mobile liquid, having a faint odour of garlic, and is freely soluble in water, alcohol, and ether; it becomes viscid at $\sim 20°$ and boils at 118—119° under 17 mm. pressure.

Aceto-$\beta\gamma$-dibromopropylamide, $CH_2Br\cdot CHBr\cdot CH_2\cdot NHAc$, which is formed when bromine is added to a cooled solution of acetoallylamide in carbon tetrachloride, separates during the addition as a viscid, gum-like mass; it crystallises from ethylic acetate in silvery leaflets melting at 134° (uncorr.), dissolves in warm carbon tetrachloride and chloroform, and readily in alcohol and water, but is insoluble in benzene, ether, and light petroleum; it is very hygroscopic, and readily loses hydrogen bromide; it appears to crystallise with $1H_2O$.

γ-Amido-$\alpha\beta$-propylenic glycol, $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NH_2$, prepared by boiling acetodibromopropylamide with water during 24 hours, is a very hygroscopic, viscid liquid, which decomposes when distilled; it dissolves readily in water and alcohol, but is insoluble in ethylic acetate, ether, and benzene; when decomposed with nitrous acid, it yields glycerol. Its salts are very hygroscopic, and their solutions give a white, flocculent precipitate with mercuric chloride. Gold chloride is rapidly reduced by the aqueous solution of the hydrochloride. The *platinochloride*, $(C_3H_7O_2\cdot NH_2)_2,H_2PtCl_6$, crystallises in golden yellow, shining needles, dissolves with exceptional readiness in water and alcohol, and melts at 185° (uncorr.).

γ-Ethylamido-$\alpha\beta$-propylenic glycol, $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NHEt$, obtained by the action of ethylic iodide on the amido-glycol, is a thick, colourless liquid which boils at 141—142° under 18 mm. pressure; it is very readily soluble in water and alcohol, but insoluble in

ether, benzene, ethylic acetate, and chloroform. It dissolves in acids with evolution of heat. *γ-Ethylamido-αβ-propylenic diacetate*, $OAc \cdot CH_2 \cdot CH(OAc) \cdot CH_2 \cdot NHEt$, obtained on warming the amido-glycol with acetic anhydride, is an odourless liquid boiling at 189—190° under 16 mm. pressure; it is miscible in all proportions with water and alcohol, but is only sparingly soluble in benzene, ether, and similar solvents.

When allylamine dibromide is treated with alcoholic potash, a *substance* having the composition $C_6H_{12}N_2O$ or $C_6H_{11}NO_2$ is produced in small quantities. This is a pale yellow, oily liquid, having a slight odour of pyridine; it boils at 112—113° under 16 mm. pressure, and dissolves readily in water, alcohol, and benzene, but somewhat sparingly in ether.   A. L.

Triethylamine Oxide. By ARTHUR LACHMAN (*Ber.*, 1899, **32**, 27). —Contrary to Hantzsch's statement, (Abstr., 1898, i, 623), this compound does exist, and can be distilled without decomposing; it boils at 152—158°. It was prepared from nitroethane and zinc ethyl.
                                                        C. F. B.

Methylethylpropylisobutylammonium Base. By WILHELM MARCKWALD and ALBERT (FREIHERR) VON DROSTE-HUELSHOFF (*Ber.*, 1899, **32**, 560—564).—Theoretically, this base is of great interest since, by the action of moulds, Le Bel seems to have obtained an optically active substance from its chloride, the activity being due to the presence of an asymmetrical quinquevalent nitrogen atom in the molecule. The present paper deals with a repetition of the work with results which are not in accordance with those obtained by Le Bel.

Starting with commercial ethylamine, paratoluenesulphonethylamide was first prepared by means of paratoluenesulphonic chloride and sodium hydroxide; this, on treatment with alcoholic potassium hydroxide and isobutylic bromide, was converted into paratoluene-sulphonethylisobutylamide, which, on decomposition with chloro-sulphonic acid, yielded *ethylisobutylamine*, a mobile liquid boiling at 98°, the *nitroso*-compound of which boils at 193°; the *chloride* forms stable, white crystals, and melts and decomposes at 209°, and the *platinochloride* melts at 201°.

On boiling with sodium methylic sulphate in aqueous solution, this base was further converted into *methylethylisobutylamine*, a liquid boiling at 105°; its *chloride* is hygroscopic, its *platinochloride* melts at 197°, and its *aurochloride* at 99°. *Methylethylpropylisobutylammonium iodide*, prepared quantitatively by the addition of propylic iodide to this base, melts at 196·5°; the *platinochloride* melts with decomposition at 236°, and the *aurichloride* at 103°.

All attempts to obtain an optically active substance from this compound were failures. The authors are further engaged in investigating the asymmetry of the quinquevalent nitrogen atom when combined with five different radicles.   J. F. T.

Ethylideneimine. By MARCEL DELÉPINE (*Compt. rend.*, 1899, **128**, 105—108. Compare Abstr., 1898, i, 462).—As the author has previously shown, aldehyde-ammonia may be regarded as the hydrate of ethylideneimine, which appears from the following considerations

to have the constitution $\text{CHMe}\underset{\text{NH·CHMe}}{\overset{\text{NH·CHMe}}{<}}\text{NH}$. That aldehyde-ammonia is a hydrate is proved by its conversion into ethylideneimine when placed in a vacuum over sulphuric acid, and also by the fact, noticed by Liebig, that silver nitrate in aqueous solution yields with aldehyde-ammonia a salt of the formula $(C_2H_5N)_3,1\frac{1}{2}AgNO_3$, which contains no water. The formation of the substance $\text{CHMe}(NHBz)_2$, which Limpricht obtained by the action of benzoic chloride on aldehyde-ammonia, indicates that a CHMe-group is united with two nitrogen atoms. From aldehyde-ammonia, Curtius has obtained nitrosoparaldimine, $C_6H_{12}O_2{:}N{\cdot}NO$, the formation of which points to the existence of an imido-group, and the author has obtained the corresponding chlorine derivative by the action of sodium hypochlorite. *Chloroparaldimine*, $\text{CHMe}\underset{\text{O·CHMe}}{\overset{\text{O·CHMe}}{<}}\text{NCl}$, is an unstable oil, having a powerful odour, and is soluble in ether. In the presence of acetic acid, however, instead of this oil, a *substance* is obtained which crystallises in needles soluble in ether, and appears to have the composition $\text{CHMe}\underset{\text{NCl·CHMe}}{\overset{\text{NCl·CHMe}}{<}}\text{NCl}$. A lower homologue of this substance, prepared in a similar manner and having the formula $(CH_2{:}NCl)_3$, has been already described by the author. When an alcoholic solution of ethylideneimine is treated with hydrogen sulphide, it yields the theoretical quantity of thialdine, a compound which is also formed by the action of ammonia on thialdehyde, and is known to have the constitution $\text{CHMe}\underset{\text{S·CHMe}}{\overset{\text{S·CHMe}}{<}}\text{NH}$. An intermediate *compound*, probably $\text{CHMe}\underset{\text{NH·CHMe}}{\overset{\text{S——CHMe}}{<}}\text{NH}$, was also obtained; it forms a crystalline hydrate melting at 70°, and is converted into thialdine by the further action of hydrogen sulphide.

It should be noted that in the majority of reactions, the tri-polymerised forms of aldehyde-ammonia and of ethylideneimine are involved, but that depolymerisation sometimes occurs. Such is the case when the compounds are volatilised or left in aqueous solution, and in certain chemical reactions as, for instance, the formation of carbothialdine, $CS_2(CHMe{:}NH)_2$.　　　　　　　　　　　　　　　　　N. L.

Stability of Stereoisomeric Oximes in Presence of Acids and Alkalis. By RICHARD ABEGG (*Ber.*, 1899, 32, 291—297).— Whilst the oxime radicle acts as a base in acid or neutral solution, and therefore receives the $+$ charge of a cation when dissociated electrolytically, it becomes the anion in an alkaline solution, and receives a $-$ charge. The supposition is made, therefore, that the form I will be the more stable in alkaline solution, and the form II in acid solution, when the radicle R_1 is electropositive compared with R_2.

I. $\underset{(-)HON}{\overset{(+)R_1\ \underset{\|}{C}\cdot R_2(-)}{}}$ 　II. $\underset{NOH(+)}{\overset{(+)R_1\cdot\underset{\|}{C}\cdot R_2(-)}{}}$.
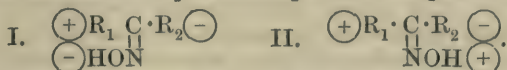
Four examples are quoted in support of this theory.　　T. M. L.

Action of Ethylenediamine on Isobutaldehyde, Isovaler-aldehyde, Acetaldehyde, and Glyoxal. By EDMUND KOLDA (*Monatsh.*, 1898, **17**, 609—626).—Ethylenediamine readily reacts with isobutaldehyde, forming a condensation product, $C_{10}H_{20}N_2$, which is a thick, colourless liquid boiling at 87—89° under 18 mm. pressure, and has strongly basic properties. It is decomposed by boiling water, forming ethylenediamine and isobutaldehyde, and is also decomposed by bromine, yielding ethylenediamine hydrobromide. The *platinochloride* is an amorphous, yellow powder. The condensation product of isovaleraldehyde and ethylenediamine boils at 123—125° under 20 mm. pressure, and resembles the foregoing compound in its properties; the *platinochloride* is an amorphous, yellow powder. When ethylenediamine reacts with acetaldehyde, a portion of the latter is converted into aldol, which reacts with acetaldehyde and ethylenediamine in molecular proportion, forming a product, $CHMe:N\cdot C_2H_4\cdot N:CH\cdot CH_2\cdot CHMe\cdot OH$, which crystallises in large rhombohedra, melts at 111—113° and forms an amorphous, yellow *platinochloride*. When boiled with water, the condensation product decomposes, yielding ethylenediamine and a resinous mass, the odour of aldehyde and crotonaldehyde being noticed during the decomposition. Glyoxal reacts with ethylenediame forming an amorphous mass which melts at 145—146°, and probably has the constitution

$$CHO\cdot CH{\large<}^{NH\cdot C_2H_4\cdot N:CH}_{NH\cdot C_2H_4\cdot N:CH}.$$ This substance is decomposed by boiling water, and yields a reddish-brown, amorphous *platinochloride*.

<div align="right">A. H.</div>

Action of Potassium Cyanide on Aliphatic Aldehydes. By LEOPOLD KOHN (*Monatsh.*, 1898, **19**, 519—523).—Potassium cyanide acts on many aliphatic aldehydes, producing condensation products of the aldol type; thus propaldehyde and valeraldehyde yield the corresponding aldols, whilst acetaldehyde suffers further change, and is converted into a substance of higher molecular weight.

When isobutaldehyde is treated with potassium cyanide, *isobut-aldol cyanhydrin*, $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CH(OH)\cdot CN$, is produced; the formation of this substance is accounted for by the fact that isovaleric acid is a product of the reaction, and this liberates hydrogen cyanide, which attacks the isobutaldol formed, in the usual manner. The cyanhydrin crystallises in measurable, colourless tablets, and melts at 140°; it is insoluble in water and ether, but dissolves in hot alcohol. When treated with potash, it yields isobutyric acid, potassium cyanide, and *octylic glycol*, $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH$; the last-named crystallises in tables and melts at 51·5°.

On hydrolysis, the cyanhydrin yields a crystalline *hydroxy-γ-lactone*, $C_9H_{16}O_3$, which dissolves readily in alcohol and ether, melts at 92·5°, and, on treatment with alkalis, yields salts of the corresponding dihydroxy-acid; the *acetate* forms measurable crystals, and melts at 59°. When oxidised by potassium permanganate, the hydroxy-lactone yields isobutyric acid and a ketonic acid, possibly isobutyryl-formic acid, the formation of these substances being probably preceded

by that of the αγ-diketonic acid, $CHMe_2 \cdot CO \cdot CMe_2 \cdot CO \cdot COOH$, which would give these two products on hydrolysis.   A. L.

Action of Hydrazine Hydrate on Isobutaldol. By Adolf Franke (*Monatsh.*, 1898, **19**, 524—535).—Hydrazine hydrate, in 50 per cent. aqueous solution, reacts with pure isobutaldol at 60°, and the product may be separated by fractional distillation into two portions, boiling at 163—165° and at 230° respectively. The former, which is *isobutaldazine*, $N_2(:CH \cdot CHMe_2)_2$, may also be obtained by the action of isobutaldehyde on hydrazine hydrate; it is a pale yellow oil having a penetrating odour. Its solution, in dilute hydrochloric acid, colours woody tissue an intense yellow, and, in this respect, it resembles pyrazoline derivatives, but it does not give Knorr's pyrazoline reaction. When the aldazine, dissolved in chloroform, is treated with bromine at − 10°, hydrogen bromide is evolved, but crystalline products could not be isolated. The *hydrochloride*, $C_8H_{16}N_2,HCl$, is readily soluble in water and alcohol, sparingly so in cold alcohol, and insoluble in ether; it forms beautiful crystals and melts at 149°; its boiling aqueous solution has a distinct camphor-like odour. The *platino-chloride*, $(C_8H_{16}N_2)_2,H_2PtCl_6$, a sulphur-yellow, flocculent precipitate, melts and decomposes at 146°. The *argentonitrate*, $C_8H_{16}N_2,AgNO_3$, is obtained as a white, crystalline precipitate when silver nitrate is added to the aqueous solution of the aldazine; it is sparingly soluble in cold, but readily in hot water, and, on adding ammonia to the solution, metallic silver is precipitated.

When the hydrochloride is treated with dilute aqueous soda, a *compound*, $C_8H_{16}N_2$, isomeric with the aldazine, is obtained in quantitative amount; it is a colourless oil having the odour of camphor, and boils at 192°; it does not form a crystalline hydrochloride or argentonitrate, and, when boiled with dilute sulphuric acid, does not yield isobutaldehyde and hydrazine, but gives products the investigation of which is being continued.

Di-isobutylhydrazine, $N_2H_2(CH_2 \cdot CHMe_2)_2$, obtained when isobutaldazine is reduced with sodium and alcohol, boils at 170—175°, and has the odour and properties of an amine; the *hydrochloride*, $C_8H_{20}N_2,2HCl$, melts and decomposes at 175°. Isobutylamine is also a product of the reduction of isobutyraldazine.   A. L.

Derivatives of Synthetic Methylheptenone. By Georges Léser (*Compt. rend.*, 1899, **128**, 108—110).—*Methylhexenonepyruvic acid*, or *8-methyl-7-nonene-2 : 4-dionoic acid*, is readily obtained by the action of sodium ethoxide and ethylic oxalate on methylheptenone, and crystallises in fine, colourless prisms melting at 39—50° (?), and very soluble in most organic solvents, with the exception of cold carbon bisulphide. It forms well-crystallised salts, from which the acid is not liberated by acetic acid; the silver salt crystallises in silky needles, which become coloured on exposure to light. When ethereal solutions of methylhexenonepyruvic acid (1 mol.) and of aniline (2 mols.) are mixed, a mass of crystals is obtained, probably of the aniline salt of the acid; this, however, cannot be isolated, as the crystals rapidly lose water and are converted into the aniline salt of the *phenylimide*, $CMe_2:CH \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot C(NPh) \cdot COONH_3Ph$. This sub-

stance melts at 82°, and at the same time loses $2H_2O$, and is converted into a compound melting at 152°, which probably has the constitution
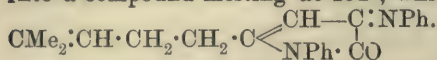
$$CMe_2:CH\cdot CH_2\cdot CH_2\cdot C\!\!<\!\!\begin{array}{l}CH\!-\!C:NPh.\\NPh\cdot CO\end{array}$$ The same compound is ob-

tained by boiling a solution, in methylic alcohol, of the aniline salt of the phenylimide, and also by the direct action of aniline on methylhexenonepyruvic acid at 100°, or at the boiling point of aniline. In the cold, ammonia behaves towards methylhexenonepyruvic acid like aniline, yielding the ammonium salt of an imido-acid; but, on warming the solution, ammonia is evolved. This reaction will be further studied.

When heated at 90—100°, methylhexenonepyruvic acid loses carbonic anhydride and is converted into *methyloctenonal*, $CMe_2:CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot CHO$, which is more readily prepared by the action of ethylic formate on methylheptenone in presence of sodium ethoxide. This compound, the first β-ketonic aldehyde isolated, crystallises from alcohol in colourless, nacreous tablets, melting at 73°, and having an agreeable odour resembling that of citronellal. It yields, with cupric acetate, a salt, $Cu(C_9H_{13}O_2)_2$, which will be subsequently described.　　　　　　　　　　　　　　　　N. L.

Action of Chlorine on Isobutylacetic Acid. By CLEMENTE MONTEMARTINI (*Gazzetta*, 1898, **28**, ii, 290—295).—The author finds that when isobutylacetic acid is chlorinated under the conditions employed in his previous work on the chlorination of isovaleric acid (Abstr., 1898, i, 236), the principal product is γ-chlorisobutylacetic acid; in this case, as also with isovaleric acid (*loc. cit.*) and isobutyric acid (Balbiano, Abstr., 1879, 615), the tertiary hydrogen atom is replaced, and from these results the author concludes that when chlorine acts, under the direct influence of the sun's rays and at a temperature of about 100°, on a monobasic acid containing the group $CHMe_2$, the hydrogen atom of the CH-group is always replaced, no matter what may be its distance from the carboxyl group.　　　　　T. H. P.

Oleodistearin, and the Iodine Number. By ROBERT HENRIQUES and HERM. KÜNNE (*Ber.*, 1899, **32**, 387—394).—Doubt having been cast on Heise's statement that the glyceride extracted from Mkani fat is oleodistearin (*Arbeit kaiserl. Gesundheitsamt*, 1896, 540), the authors have reinvestigated this substance, and find that Heise's view is correct.

Oleodistearin, $C_3H_5(C_{18}H_{35}O_2)_2(C_{18}H_{33}O_2)$, crystallises from a mixture of alcohol and ether in small, snow-white crystals melting at 45—46° and having an iodine number of 28·8; when treated in ethereal solution with an alcoholic solution of iodine chloride, it yields a *chloriodo*-additive product melting at 44·5—45·5°, and closely resembling oleodistearin, both in its behaviour towards solvents and in the fact that, when fused and resolidified, it melts 3—4° lower than before. This additive product is remarkably stable both towards acid and alkali, and only on heating in sealed tubes at 150° with alcoholic ammonia are the halogens completely eliminated and the glyceride reformed.

Like oleic acid, oleodistearin can undergo the elaidin rearrangement, although it does not do so as readily. When the red nitrous fumes from a mixture of nitrite and sulphuric acid are conducted into the melted glyceride, crystals of *elaidodistearin* are formed; this, after recrystallisation from a mixture of alcohol and ether, melts at 61° and closely resembles oleodistearin, but is less soluble in the ordinary solvents; with an alcoholic solution of iodine chloride, it forms a *chloriodo*-compound which separates from a mixture of alcohol and ether in crystals melting at 57—58°. J. F. T.

Two Modifications of Ethylic β-Aminocrotonate. By ROBERT BEHREND (*Ber.*, 1899, **32**, 544—546).—There are two modifications of ethylic β-aminocrotonate, melting at 20° and at 33° respectively; the former is produced when ethylic acetoacetate is treated with gaseous ammonia at 60°, the latter when a cooled ethereal solution of the ethylic salt is saturated with ammonia in the presence of ammonium nitrate. The conversion of one form into the other can be effected as often as required, since, on crystallising at temperatures below 19°, the form of lower melting point separates, whilst in contact with a crystal of the form of higher melting point the other modification separates. Further, on touching the crystals melting at 20° with the form of higher melting point, they are converted into the latter with development of heat. J. F. T.

Condensation of the Fatty Aldehydes with Propionic Acid. By FRANZ KIETREIBER (*Monatsh.*, 1898, **19**, 727—737).—Isobutaldehyde, sodium propionate, and propionic anhydride react at 190—200°, forming *methylisobutylideneacetic acid*, $CHMe_2 \cdot CH:CMe \cdot COOH$, in small amount; it is a colourless, oily liquid which boils at 115—116° under 15 mm. pressure. The *calcium* salt crystallises in silky needles, whilst the *silver* salt is a crystalline precipitate. With bromine, the acid yields a *dibromide*; this forms yellowish-white crystals, melts at 73°, and is converted by alkalis into the corresponding *dihydroxy*-acid, which crystallises in white plates melting at 114—115°. Acetaldehyde reacts with sodium propionate and propionic anhydride in the normal manner, tiglic acid, $CHMe:CMe \cdot COOH$, being produced, but with œnanthaldehyde there was no reaction.

A. H.

Chlorides of Monethylic Salts of Dibasic Acids. By EDMOND E. BLAISE (*Compt. rend.*, 1899, **128**, 183—185).—When the chloride of a monethylic salt of a dibasic acid, $COCl \cdot R'' \cdot COOEt$, is distilled, it partially decomposes into the normal alkylic salt and the dichloride of the acid, together with some anhydride and ethylic chloride, these reactions being also reversible. The author has therefore endeavoured to prepare these chlorides at a low temperature. When sodium ethoxide is added gradually to an alcoholic solution of the anhydride of the acid, cooled in ice, the product consists entirely of the sodium alkylic salt. The alkylic hydrogen salt is separated by acidifying the aqueous solution of the sodium alkylic salt, and after being dried over sulphuric acid is heated at about 60° for an hour with the calculated quantity of phosphorus trichloride. The monochloride thus obtained

is treated directly with zinc methyl. In this way, dimethyllevulinic acid, COMe·CMe$_2$·CH$_2$·COOH, and dimethylhexanonoic acid, COMe·CMe$_2$·CH$_2$·CH$_2$·COOH, have been prepared identical with those obtained by the oxidation of campholene and β-campholenic acid respectively. C. H. B.

Isobutylsuccinic Acid. By EDVARD HJELT (*Ber.*, 1899, **32**, 529).—Isobutylsuccinic acid (Fittig and Burwell, Fittig and Thron, this vol., i, 336 and 337), when crystallised from benzene, melts at 105°, but at 107° when crystallised from water. The *paratolilic acid* and *paratolil* of isobutylsuccinic acid melt at 135—136° and 104—108° respectively. M. O. F.

Transformation of Unsaturated Acids. By RUDOLPH FITTIG (*Annalen*, 1899, **304**, 117—145).—The paper summarises the experimental results described in the following abstracts.

M. O. F.

Itaconic, Citraconic, and Mesaconic Acids.—By RUDOLPH FITTIG and CHARLES FORD LANGWORTHY (*Annalen*, 1899, **304**, 145—156. Compare Abstr., 1893, i, 189).—Contrary to the statement of Franz (Abstr., 1894, i, 404), itaconic acid does not pass over in a current of steam, and hence may be separated with mesaconic acid from the isomeric citraconic acid which is volatile in steam. The barium salt contains $\frac{1}{2}$H$_2$O; 100 parts of the aqueous solution saturated at 20° contain 7·61 parts of the anhydrous salt.

Citraconic acid crystallises in thin, flattened needles when petroleum is added to its solution in ether; it melts and decomposes at 91°. In the purified state, it undergoes no change in the desiccator, but when impure it becomes transformed into itaconic acid. The barium salt contains 2$\frac{1}{2}$H$_2$O; 100 parts of the aqueous solution saturated at 12° contain 0·29 part of the anhydrous salt.

Barium mesaconate contains 4H$_2$O; 100 parts of the aqueous solution saturated at 15·5° contain 4·6 parts of the anhydrous salt.

When a 25 per cent. solution of bromine in chloroform is added to citraconic acid dissolved in a mixture of ether and chloroform, and the liquid exposed to sunlight, mesaconic acid is quickly precipitated; the transformation takes place more slowly under the influence of diffused light, or when aqueous solutions are employed, and does not take place at all in the dark. The analogous transformation of maleic into fumaric acid has been ascribed by Wislicenus to the addition and removal of hydrogen bromide arising from secondary reactions; this explanation does not apply in the present instance, however, because hydrogen bromide has no influence on citraconic acid dissolved in a mixture of ether and chloroform, even when exposed to direct sunlight.

The action of a boiling 10 per cent. solution of caustic soda converts itaconic acid into mesaconic acid to the extent of about 80 per cent.; this action is reversible, nearly 20 per cent. of itaconic acid being obtainable from mesaconic acid. By the same agency, citraconic acid is converted into mesaconic and itaconic acid, in quantities amounting to 60 per cent. and 20 per cent. respectively.

When itaconic acid is reduced, in acid solution, with sodium amalgam, it is converted into pyrotartaric acid to the extent of about 94 per cent.　　　　　　　　　　　　　　　　　　　　　　　M. O. F.

Pyrocinchonic Acid and its Isomerides. By RUDOLPH FITTIG and ARTHUR KETTNER (*Annalen*, 1899, **304**, 156—178. Compare Abstr., 1896, i, 599).—Experimental details of the conversion of pyrocinchonic (dimethylmaleic) acid into β-methylmesaconic and β-methylitaconic acids are described in this paper (compare *loc. cit.*).

The *silver* salt of dimethylfumaric (β-methylmesaconic) acid is crystalline , the *calcium* salt contains $2H_2O$, and the barium salt $2\frac{1}{2}H_2O$. When dimethylfumaric acid is distilled, it is, in part, converted into pyrocinchonic anhydride, which is also formed on treating the acid with acetic chloride.

The *silver* salt of methylitaconic acid is scarcely soluble in water ; the *calcium* salt is crystalline, and contains $1H_2O$. Distillation converts the acid into pyrocinchonic anhydride, but hot acetic chloride gives rise to methylitaconic *anhydride*, $C_6H_6O_3$, which crystallises from carbon bisulphide in small, lustrous leaflets and melts at 62—63° ; when distilled, the anhydride yields pyrocinchonic anhydride, and warm water converts it into methylitaconic acid.

Although bromine converts citraconic acid into mesaconic acid (preceding abstract), dimethylfumaric acid is transformed by the halogen, under the same conditions, into pyrocinchonic anhydride, the anhydride of dimethylmaleic acid. Methylitaconic acid, on the other hand, gives rise to the *dibromide*, $C_6H_8Br_2O_4$, which crystallises from ether, and melts at 153°, when it decomposes.

A boiling solution of caustic soda leaves dimethylfumaric acid, for the most part, unchanged ; methylitaconic acid, however, yields 50 per cent. of pyrocinchonic anhydride, and 28 per cent. of dimethylfumaric acid. Towards nascent hydrogen, furnished by sodium amalgam in feebly alkaline solution, dimethylfumaric and methylitaconic acids behave alike ; both yield a mixture of *cis*- and *trans*-dimethylsuccinic acids.　　　　　　　　　　　　　　　　　　　　　　　M. O. F.

Ethylitaconic Acid and its Isomerides. By RUDOLPH FITTIG and FRITZ GLASER (*Annalen*, 1899, **304**, 178—194. Compare Abstr., 1893, i, 189).—The *ethylic* salt of ethylparaconic acid boils at 278—279°, and does not solidify at −18° ; it is converted into ethylitaconic acid under the influence of sodium ethoxide.

Ethylitaconic acid, $CH_2Me\cdot CH:C(COOH)\cdot CH_2\cdot COOH$, which melts and decomposes at 162—167°, is readily soluble in hot water, but requires 74 parts of cold water to dissolve it. The *barium* salt contains $2H_2O$, and the *calcium* salt $1H_2O$, the *silver* salt being anhydrous.

Ethylcitraconic acid, $CH_2Me\cdot CH_2\cdot C(COOH):CH\cdot COOH$, crystallises from petroleum in aggregates of needles and melts at 93—95°, forming the anhydride. The *barium* salt contains $\frac{1}{2}H_2O$, and the *calcium* salt $1H_2O$, whilst the *silver* salt is anhydrous. The *anhydride*, produced when ethylcitraconic acid is submitted to dry distillation, is a yellow oil which boils at 240—245°. When aqueous ethylcitraconic acid is boiled during 2 hours in a reflux apparatus, it is, in part, converted into ethylitaconic acid.

Ethylmesaconic acid, $CH_2Me\cdot CH_2\cdot C(COOH)\!:\!CH\cdot COOH$, is obtained from ethylcitraconic acid under the influence of nitric acid, or by the action of bromine in direct sunlight; it melts at 174—175°, and dissolves in 90 parts of cold water. The *barium* and *silver* salts are anhydrous, and crystallise in needles.

The three foregoing acids are converted into propylsuccinic acid by the action of sodium amalgam.

Ethylitadibromopyrotartaric acid, $C_7H_{10}Br_2O_4$, prepared by the action of bromine dissolved in chloroform on ethylitaconic acid, melts and decomposes at 153—154°. When the viscous mother liquor is boiled with water and distilled, two acids are obtained; the non-volatile substance is probably *ethaconic acid*, $C_7H_8O_4$, melting at 145—146°. *Bromohexenoic* (β-*bromohydrosorbic*) *acid*, $CH_2Me\cdot CH\!:\!CBr\cdot CH_2\cdot COOH$, distils in an atmosphere of steam, and is formed by the elimination of the elements of carbonic anhydride and hydrogen bromide from ethylitadibromopyrotartaric acid; it crystallises from water in nacreous leaflets, melts at 51—52°, and on reduction with sodium amalgam, yields hydrosorbic acid.

Ethylitabromopyrotartaric acid, $C_7H_{11}BrO_4$, obtained by the action of hydrogen bromide on ethylitaconic acid, crystallises from water in small prisms and melts at 145—146°, losing hydrogen bromide; boiling water converts it into ethylparaconic acid.

Ethylcitrabromopyrotartaric acid, $C_7H_{11}BrO_4$, prepared by the action of hydrogen bromide on ethylcitraconic acid, melts at 119—121°; it is distinguished from its isomeride by the high degree of solubility in water and in warm chloroform. M. O. F.

Dimethylitaconic (Teraconic) Acid and its Isomerides. By RUDOLPH FITTIG and HERMANN KRAFFT (*Annalen*, 1899, **304**, 195—207).

—Teraconic acid is obtained by the action of sodium ethoxide on the ethylic salt of terebic acid. The *anhydride*, produced on heating the acid at 200°, crystallises from carbon bisulphide in lustrous leaflets; it melts at 44° and boils at 197° and 275—283° under pressures of 22 mm. and 760 mm. respectively.

Dimethylcitraconic acid, $CHMe_2\cdot C(COOH)\!:\!CH\cdot COOH$, crystallises from petroleum in aggregates of needles and melts at 91—93°, when it decomposes; the *barium* salt contains $1\frac{1}{2}H_2O$, and the *calcium* salt $1H_2O$, the *silver* salt being anhydrous. The *anhydride* is produced with teraconic anhydride when teraconic acid is distilled under atmospheric pressure.

Dimethylmesaconic acid, $CHMe_2\cdot C(COOH)\!:\!CH\cdot COOH$, prepared by the action of bromine in chloroform on dimethylcitraconic acid, crystallises from water and melts at 185°; it is identical with Demarçay's iso-oxyhexic acid, prepared from ethylic isopropylacetoacetate by Walden's method. The *barium* salt contains $4H_2O$, and the *calcium* salt $2H_2O$; the *silver* salt crystallises from boiling water in aggregates of small needles. When dimethylmesaconic acid is submitted to dry distillation, it yields 21 per cent. of dimethylcitraconic acid and 12 per cent. of teraconic acid; dimethylcitraconic acid is also converted into teraconic acid when heated with water in sealed tubes at 150—160°. The foregoing acids are comparatively indifferent

towards boiling aqueous alkalis; sodium amalgam reduces them to isopropylsuccinic acid. M. O. F.

Dimethylaticonic Acid. By RUDOLPH FITTIG and NICOLAUS PETKOW (*Annalen*, 1899, **304**, 208—240).—*Dimethylaticonic acid*, $CH_2:CMe\cdot CH(COOH)\cdot CH_2\cdot COOH$, prepared by the action of a boiling 20 per cent. solution of caustic soda on teraconic acid, is separated from the latter with considerable difficulty; it separates from water in aggregates of small crystals, and melts at 146—147°. The acid dissolves more readily than teraconic acid in water and in ether, 100 parts of the former solvent at 15° dissolving 1·49 parts of teraconic acid and 7·56 parts of dimethylaticonic acid; 100 parts of ether at 15° dissolve 1·37 parts and 19·47 parts of the respective acids. The *calcium* salt contains $2H_2O$, and the *barium* salt $1H_2O$; the *anhydride*, obtained by distilling the acid at 170—200° under 20 mm. pressure, remains viscous at −20°. Boiling water resolves dimethylaticonic acid into isocaprolactone, terebic acid, and a small proportion of teraconic acid; boiling dilute sulphuric acid converts it into terebic acid, whilst a boiling 20 per cent. solution of caustic soda regenerates teraconic acid.

Bromisoterebic acid, $C_7H_9BrO_4$, obtained by the action of bromine in chloroform on dimethylaticonic acid, melts at 130—131°, and separates from water in large, lustrous crystals belonging to the rhombic system: $a : b : c = 0.9702 : 1 : 0.7846$. *Isoheptodilactone*, $C_7H_8O_4$, prepared from bromisoterebic acid by the action of alkalis, melts at 115°, and is converted by alkalis into the salts of a dibasic dihydroxy-acid; the *barium* salt contains $1H_2O$, and the calcium salt $1\frac{1}{2}H_2O$, whilst the *silver* salt is anhydrous. *Hydroxyisoterebic acid*, $C_7H_{10}O_5$, another product of the action of alkalis on bromisoterebic acid, melts at 163°, and is identical with the compound obtained by Roser from chloroterebic acid; it separates from water in highly lustrous crystals belonging to the monoclinic system: $a : b : c = 0.8870 : 1 : 0.8241$; $\beta = 88° 29' 35''$. The *barium* salt contains $1H_2O$, and the *calcium* salt $\frac{1}{2}H_2O$; the *silver* salt separates from water in small, colourless crystals. Prolonged treatment with concentrated boiling alkalis resolves hydroxyisoterebic acid into the salts of the dibasic acid derived by the same method from isoheptodilactone.

Isoterebilenic acid, $C_7H_8O_4$, is obtained by boiling an aqueous solution of isoheptodilactone during 10 hours, evaporating the solution, and removing the unchanged lactone which separates; it is also produced in small amount when hydroxyisoterebic acid is heated with fuming hydrogen bromide in sealed tubes at 100—120°. It melts at 118—119°, and forms large crystals belonging to the monoclinic system: $a : b : c = 1.147 : 1 : 1.510$; $\beta = 78° 57'$. The *barium* salt contains $1H_2O$, and the *calcium* salt $\frac{1}{2}H_2O$; the *silver* salt separates from water in well-formed crystals.

Isoterebic (dimethylisoparaconic) acid, $C_7H_{10}O_4$, prepared by reducing isoterebilenic acid with sodium amalgam, is insoluble in petroleum and melts at 77—78°; the *calcium* salt contains $1H_2O$, and the *barium* and *silver* salts are anhydrous. Isoterebic acid is resolved by barium

hydroxide into a salt of the acid $C_7H_{12}O_5$, corresponding with diaterebic acid; the *barium* and *silver* salts are anhydrous. M. O. F.

Propylitaconic Acid and its Isomerides. By RUDOLPH FITTIG and FRITZ FICHTER (*Annalen*, 1899, **304**, 241—258).—Propylitaconic acid, $CHPr^a{:}C(COOH){\cdot}CH_2{\cdot}COOH$ (compare Abstr., 1890, 589), prepared by the action of sodium ethoxide on ethylic propylparaconate, melts and decomposes at 159—160·5°; the *calcium* salt contains $1H_2O$, and the *barium* salt is anhydrous. When the acid is heated with fuming hydrochloric acid in a sealed tube at 120°, propylparaconic acid is regenerated.

Propylcitraconic acid, $CH_2Pr^a{\cdot}C(COOH){:}CH{\cdot}COOH$, obtained on distilling propylitaconic acid, crystallises from a mixture of ether and petroleum in transparent plates and melts at 80°, forming the anhydride; the *calcium* salt contains $1H_2O$, whilst the *barium* and *silver* salts are anhydrous. When heated with water in a sealed tube at 160°, propylcitraconic acid is converted into propylitaconic acid.

Propylmesaconic acid, $CH_2Pr^a{\cdot}C(COOH){:}CH{\cdot}COOH$, produced on treating propylcitraconic acid in chloroform with a solution of bromine in the same medium, crystallises from water in slender needles and melts at 170°; it boils at 240° under a pressure of 16 mm. The *calcium* salt contains $2H_2O$, and the *barium* salt $1H_2O$; the *silver* salt is somewhat readily soluble in hot water, and resists the action of light.

The three acids yield butylsuccinic acid on reduction with sodium amalgam. A boiling 20 per cent. solution of caustic soda leaves propylitaconic acid for the most part unchanged, giving rise to a small quantity of aticonic acid; propylcitraconic acid yields 43 per cent. of propylitaconic acid, which is also formed in considerable amount when caustic soda acts on propylmesaconic acid. M. O. F.

Isopropylitaconic Acid and its Isomerides. By RUDOLPH FITTIG and ARTHUR W. BURWELL (*Annalen*, 1899, **304**, 259—280).—The *ethylic* salt of isopropylparaconic acid remains liquid at − 19°, and boils at 282°.

Isopropylitaconic acid, $CHPr^\beta{:}C(COOH){\cdot}CH_2{\cdot}COOH$, obtained by the action of sodium ethoxide on ethylic isopropylparaconate, separates from water in nacreous crystals and melts at 189—192°, when it becomes brown, and liberates gas. The *barium* salt contains $2H_2O$, and the *calcium* salt $1H_2O$; the *silver* salt is indifferent towards light.

Isopropylcitraconic acid, $CH_2Pr^\beta{\cdot}C(COOH){:}CH{\cdot}COOH$, obtained in the form of anhydride by distilling isopropylitaconic acid, crystallises from a mixture of chloroform and petroleum in elongated, lustrous needles, and melts at 78—81°, forming the anhydride. The *barium* and *silver* salts are anhydrous. When an aqueous solution of the acid is heated at 150—160°, it is converted almost completely into isopropylitaconic acid.

Isopropylmesaconic acid, $CH_2Pr^\beta{\cdot}C(COOH){:}CH{\cdot}COOH$, is formed from isopropylcitraconic acid under the influence of bromine, and melts at 183°; it forms crystals belonging to the monoclinic system: $a:b:c = 1·4268:1:0·7453$; $\beta = 75° 40'$. This acid, which has been

described as oxyheptic acid by Demarçay, is formed in small amount when isopropylcitraconic acid is treated with nitric acid. The *barium* and *calcium* salts are anhydrous.

Boiling caustic soda has no action on isopropylitaconic acid, this substance being produced when isopropylcitraconic acid is treated with a boiling 10 per cent. solution of caustic soda during 30 hours; it is also formed when isopropylmesaconic acid is heated with 25 per cent. caustic soda during 35 hours. *Isobutylsuccinic acid*, $C_8H_{14}O_4$, prepared by reducing the three foregoing acids with sodium amalgam, melts at 107—108°, and forms crystals belonging to the rhombic system: $a : b : c = 0.8551 : 1 : 1.0877$.

Isopropylisoparaconic acid, $\begin{matrix} CMe_2 \cdot CH_2 \\ | \quad\quad | \\ O ——— CO \end{matrix}> CH \cdot CH_2 \cdot COOH$, is obtained

in the preparation of isopropylitaconic acid from ethylic isopropylparaconate, and is also produced when isopropylitaconic acid is heated with fuming hydrochloric acid at 125—135° during 3 hours; it crystallises from water in large, lustrous, transparent prisms belonging to the monoclinic system: $a : b : c = 0.6623 : 1 : 0.4853$; $\beta = 72°\ 54'$. It melts at 143°, and when carefully heated volatilises without decomposing. The *calcium* salt contains $3\frac{1}{3}H_2O$, whilst the *barium* and *silver* salts are anhydrous; the *ethylic* salt boils at 276°. Further treatment with alkalis resolves the salts into those of the dibasic dihydroxy-acid, $C_8H_{14}O_5$; the *calcium*, *barium*, and *silver* salts are anhydrous.

Evidence in support of the above constitutional formula for isopropylisoparaconic acid is supplied by the fact that the substance is produced from isobutylsuccinic acid by oxidation with potassium permanganate.   M. O. F.

Isopropylisoparaconic acid. By RUDOLPH FITTIG and HEINRICH THRON (*Annalen*, 1899, **304**, 280—298. Compare forgoing abstract). —The extraordinary readiness with which isopropylisoparaconic acid is produced on heating isopropylparaconic acid with fuming hydrochloric acid, would seem to indicate the existence of stereoisomerism instead of structural isomerism, but this possibility is precluded by the formation of isopropylisoparaconic acid on oxidising isobutylsuccinic acid with potassium permanganate.

Isobutylethanetricarboxylic acid, $CH_2Pr^{\beta} \cdot C(COOH)_2 \cdot CH_2 \cdot COOH$, is prepared by treating the sodium derivative of ethylic isobutylmalonate with ethylic chloracetate, and hydrolysing the ethereal salt with alcoholic potash; it crystallises in slender, silky needles on adding petroleum to the solution in ether, and melts at 156°, yielding isobutylsuccinic acid. The *calcium* salt contains $7H_2O$, and the *barium* salt $4H_2O$; the *silver* salt is crystalline, and is sensitive towards light.

Isobutylsuccinic acid, $COOH \cdot CH(CH_2Pr^{\beta}) \cdot CH_2 \cdot COOH$, obtained on heating the foregoing acid at 160° until carbonic anhydride ceases to be evolved, separates from water in large, rhombic crystals, and melts at 107°; as already stated (*loc. cit.*), oxidation converts it into isopropylisoparaconic acid.

Another method of preparing isopropylisoparaconic acid consists in heating isopropylitaconic acid with sulphuric acid. It is also produced by the action of sodium on a mixture of ethylic succinate and isobut-

aldehyde, isopropylitaconic acid being also formed. When boiled in a reflux apparatus during 10 minutes, it yields about 25 per cent. of isopropylcitraconic acid along with a smaller proportion of isopropylitaconic acid.

The *acid* $C_{16}H_{20}O_6$, obtained by heating ethylic isopropylisoparaconate with sodium and ether on the water-bath, crystallises in leaflets containing $6H_2O$, and melts at $222°$. The *calcium, barium,* and *silver* salts are anhydrous, and indicate that the acid is monobasic. The substance is very stable, resisting the action of a boiling 10 per cent. solution of caustic soda during several hours; it undergoes no change when heated at $230°$. M. O. F.

Isobutylitaconic Acid and its Isomerides. By RUDOLPH FITTIG and CARL SCHIRMACHER (*Annalen*, 1899, **304**, 298—311. Compare Fittig and Kräncker, Abstr., 1890, 874).—*Isobutylcitraconic acid,* $CH_2Pr^\beta \cdot CH_2 \cdot C(COOH)\colon CH \cdot COOH$, prepared in the form of anhydride by submitting isobutylitaconic acid to dry distillation, crystallises from a mixture of chloroform and petroleum in beautiful, colourless leaflets, and melts at $75·5$—$80°$. When pure, it remains unchanged on exposure to air, but the impure substance is resolved into the anhydride and water (compare Fittig and Weil, Abstr., 1895, i, 207). The *barium, calcium,* and *silver* salts are anhydrous.

Isobutylmesaconic acid, $CH_2Pr^\beta \cdot CH_2 \cdot C(COOH)\colon CH \cdot COOH$, obtained by the action of bromine on isobutylcitraconic acid, crystallises from water in lustrous leaflets, and melts at 205—$206°$; the *barium* and *calcium* salts contain $1H_2O$, and the *silver* salt is anhydrous.

When isobutylcitraconic acid is heated with water in a sealed tube at $160°$, it yields isobutylitaconic acid; the latter is in part converted into isobutylparaconic acid by the agency of hydrobromic acid at $100°$.

Isoamylsuccinic acid, $CH_2Pr^\beta \cdot CH_2 \cdot CH(COOH) \cdot CH_2 \cdot COOH$, prepared by reducing isobutylitaconic acid in feebly acid solution with sodium amalgam on the water-bath, dissolves very readily in water, and melts at 75—$76°$; it resembles the citraconic acids more closely than those of the succinic series. The *barium* salt contains $\frac{1}{2}H_2O$, and the *calcium* and *silver* salts are anhydrous.

A boiling 10 per cent. solution of caustic soda has no action on isobutylitaconic acid, but gives rise to the latter when boiled with isobutylcitraconic and isobutylmesaconic acids. M. O. F.

Isobutylaticonic Acid. By RUDOLPH FITTIG and EDGAR ERLENBACH (*Annalen*, 1899, **304**, 311—325).—*Isobutylaticonic acid,* $C_9H_{14}O_4$, is obtained in small quantities when isobutylitaconic acid is treated with a boiling 20 per cent. solution of caustic soda in a reflux apparatus during 15 hours; it crystallises in elongated prisms when petroleum is added to the solution in ether, and melts at $95°$. It is more readily soluble than isobutylitaconic acid, 100 parts of water dissolving $1·863$ parts and $0·377$ part respectively; 100 parts of ether dissolve $35·60$ parts and $3·01$ parts respectively. The *barium, calcium,* and *silver* salts are anhydrous. The *dibromide,* $C_9H_{14}Br_2O_4$, is formed to the extent of 16 per cent. when a solution of bromine in chloroform acts on isobutylaticonic acid in the same medium; it melts and loses hydrogen bromide at $210°$,

Bromisobutylisoparaconic acid, $C_9H_{13}BrO_4$, the chief product of the action of bromine on isobutylaticonic acid, crystallises from ether in silky, lustrous needles, and melts at 126°. *Isobutylisoparaconic acid*, $C_9H_{14}O_4$, prepared by reducing the bromo-derivative with sodium amalgam, crystallises from ether in long needles and melts at 115°; the *barium* salt contains $1H_2O$, the *calcium* salt $2H_2O$, and the *silver* salt is anhydrous.

Isobutylisaconic acid, $C_9H_{12}O_4$, obtained by the action of aqueous caustic soda on bromisobutylisoparaconic acid, melts at 51°, and dissolves readily in common solvents; the *barium* salt contains $4H_2O$, and the *calcium* salt $3H_2O$, whilst the *silver* salt crystallises from hot water in nacreous, anhydrous leaflets.

Isononodilactone, $C_9H_{12}O_4$, produced along with isobutylisaconic acid on treating bromisobutylisoparaconic acid with boiling water in a reflux apparatus during 5 hours, crystallises from water and melts at 133°; further treatment with boiling water converts the dilactone into isobutylisaconic acid.

When isobutylaticonic acid is heated with a 10 per cent. aqueous solution of caustic soda in a reflux apparatus during 10 hours, it is converted into isobutylitaconic acid to the extent of about 60 per cent.

M. O. F.

Hexylitaconic Acid and its Isomerides. By RUDOLPH FITTIG and WILLIAM D. HOEFFKEN (*Annalen*, 1899, **304**, 326—339).—The *ethylic* salt of hexylparaconic acid is a viscous liquid which boils at 325—326°.

Hexylitaconic acid, $C_6H_{13}\cdot CH:C(COOH)\cdot CH_2\cdot COOH$, obtained by heating ethylic hexylparaconate with alcoholic sodium ethoxide, and hydrolysing the product, crystallises from water in silky needles, and melts at 129—130°; the *barium* and *silver* salts are anhydrous, and the *calcium* salt contains $2H_2O$. On heating the acid with hydrobromic acid during 32 hours at the temperature of boiling water, it is in part converted into hexylparaconic acid.

Hexylcitraconic acid, $C_6H_{13}\cdot CH_2\cdot C(COOH):CH\cdot COOH$, prepared by heating the foregoing acid at 205—210° and hydrolysing the anhydride obtained, crystallises in aggregates of needles and melts at 86°; the *barium* and *silver* salts are anhydrous, and the *calcium* salt contains $1H_2O$. When heated with water in a sealed tube at 160°, hexylcitraconic acid is converted into hexylitaconic acid.

Hexylmesaconic acid, $C_6H_{13}\cdot CH_2\cdot C(COOH):CH\cdot COOH$, produced by the action of bromine on hexylcitraconic acid, dissolves in cold water with great difficulty, and melts at 153—154°; the *barium* and *silver* salts are anhydrous, and the *calcium* salt contains $1H_2O$.

When hexylitaconic acid is heated with a 10 per cent. solution of caustic soda, about 70 per cent. remains unchanged, the rest becoming converted into the *acid* $C_{11}H_{18}O_4$, which is isomeric with hexylitaconic acid, and melts at 70—74°; the same agent converts hexylcitraconic and hexylmesaconic acids into hexylitaconic acid.

Heptylsuccinic acid, $C_6H_{13}\cdot CH_2\cdot CH(COOH)\cdot CH_2\cdot COOH$, prepared by reducing the three isomeric acids with sodium amalgam, crystal-

lises from water and melts at 90—91°; the *barium* and *silver* salts are anhydrous, and the *calcium* salt contains $1H_2O$.　　　M. O. F.

Cineolic Acid. By HANS RUPE (*Chem. Centr.*, 1898, ii, 1055 ; from *Arch. Sci. phys. nat. Genève*, [iv], **6**, 388—390).—When cineolic acid, $COOH \cdot CMe {<}{\,}^{O-CMe_2}_{CH_2 \cdot CH_2}{\,}{>} CH \cdot COOH$, is heated with water at 160°, it yields *cineolenic acid*, $CHMe {<}{\,}^{O-CMe_2}_{CH_2 \cdot CH_2}{\,}{>} CH \cdot COOH$, and another acid of the same empirical formula. The former crystallises in plates or prisms, melts at 83—84°, boils at 127·5—129·5° under 13 mm., and at 250° under 760 mm. pressure ; as it is not attacked by bromine or potassium permanganate, it probably contains the cineol chain.

The second acid, $CHMe{:}CH \cdot CH_2 \cdot CH(COOH) \cdot CMe_2 \cdot OH$, crystallises from water, in which it is much more soluble than cineolic acid, in small needles, melts at 53—54°, and boils at 158—160° under 13 mm. pressure ; its magnesium salt is insoluble in cold water. This acid is also obtained by heating cineolenic acid with water at 150°, and cannot contain the cineol chain, as it is attacked by bromine and potassium permanganate. When distilled under the ordinary pressure, it loses $1H_2O$ and yields a new liquid acid, $CHMe{:}CH \cdot CH_2 \cdot CH(COOH) \cdot CMe{:}CH_2$, hence it probably contains an OH-group in the β-position.　　　E. W. W.

Polymerisation of Hydroaromatic Ketones. By EMIL KNOEVENAGEL and E. REINECKE (*Ber.*, 1899, **32**, 418—428).—Ethylic β-methylamidocrotonate readily unites with ethylic ethylideneacetoacetate at 0° to form *ethylic β-methylamidocrotonoethylideneacetoacetate*, $NHMe \cdot CMe{:}C(COOEt) \cdot CHMe \cdot CHAc \cdot COOEt$, which crystallises from light petroleum in well-formed, transparent prisms, melts at 103—104°, and is readily soluble in alcohol, ether, and benzene ; when this is boiled for 2—3 hours with 70 per cent. aqueous potash, it gives rise to a *substance*, $C_8H_{12}O$, which crystallises from light petroleum in tufts of needles, melts at 113°, boils unchanged at 185—188° under 11 mm. pressure, and with partial decomposition at 258—262° under the ordinary pressure. The same product is also obtained on boiling ethylic ethylidenebisacetoacetate, ethylic 1 : 3-dimethyl-5-cyclohexenone-2 : 4-dicarboxylate, or 1 : 3-dimethyl-5-cyclohexenone with 70 per cent. aqueous potash ; from molecular weight determinations by the cryoscopic and boiling point methods, it appears to be dimeric with the latter of these, and the formula $CH_2 {<}{\,}^{CMe=CH}_{CHMe \cdot CH_2}{\,}{>} C(OH) \cdot CH {<}{\,}^{CHMe \cdot CH_2}_{CO——CH}{\,}{>} CMe$ is attributed to it, assuming that it is formed according to the laws governing the polymerisation of open-chain ketones. In accordance with this view are the facts that it yields a *monoxime*, $C_{16}H_{25}NO_2$, and a *monophenylhydrazone*, $C_{22}H_{30}N_2O$, only, without forming a dioxime or a diphenylhydrazone ; the former of these separates from dilute alcohol in yellow crystals and melts at 197°, whilst the latter crystallises from alcohol in white needles and melts at 202—204° ; the *semi-carbazone* melts at 212°. The assumption of the presence of a

hydroxyl group, however, is not borne out by the behaviour of the compound with acetic anhydride or phenylcarbimide, since both of these are without action; phosphorus pentoxide, zinc chloride, and 30 per cent. sulphuric acid also seem incapable of causing a separation of water to form a substance of the type of mesityl oxide.

1-Methyl-5-cyclohexenone remains unchanged when heated with 70 per cent. aqueous potash, but ethylic benzylidenebisacetoacetate and 1-methyl-3-phenyl-5-cyclohexenone both give rise to the same *substance*, $C_{26}H_{28}O_2$, which crystallises from alcohol, melts at 159°, is sparingly soluble in ether, chloroform, light petroleum, and benzene, and yields an *oxime*, $C_{26}H_{29}NO_2$, which crystallises from alcohol and melts at 207°; the *phenylhydrazone* crystallises from benzene and melts at 250—251°. 1-Methyl-3-isopropylphenyl-5-cyclohexenone gives rise, when treated with alkali, to the *polymeride*, $C_{32}H_{40}O_2$, which crystallises from light petroleum, melts at 175°, and is easily soluble in chloroform and benzene. W. A. D.

Action of Iodine Chloride on Chlorobenzene in presence of Aluminium Chloride. By A. MOUNEYRAT (*Compt. rend.*, 1899, **128**, 240—242).—When iodine chloride acts on monochlorobenzene in presence of dry aluminium chloride at 55—60°, parachloriodobenzene is obtained in quantity amounting to from 25 to 30 per cent. of the calculated yield, small quantities of dichlorobenzene and trichlorobenzene being formed at the same time. C. H. B.

1 : 3 : 5-Tribromo-2 : 4 : 6-tri-iodobenzene. By CONSTANTIN I. ISTRATI (*Compt. rend.*, 1898, **127**, 519).—When a mixture of 1 : 3 : 5-tribromobenzene with concentrated sulphuric acid is heated with iodine for six or seven days, a mixture of iodine derivatives is obtained, from which, by successive treatment with various solvents, 1 : 3 : 5-*tribromo*-2 : 4 : 6-*tri-iodobenzene* may be isolated. This crystallises in small, golden-yellow needles melting at 322°, and is dissolved by boiling chloroform and boiling alcohol to the extent of 0·306 and 0·040 per cent. respectively. It is attacked with difficulty by fuming nitric acid, but, in presence of sulphuric acid, yields a mixture of nitro-derivatives containing 4·07 per cent. of nitrogen. Cold alcoholic potash, whilst not destroying the original form of the crystals, immediately converts them into a greyish-yellow substance which does not contain iodine, and is insoluble in ordinary solvents.

N. L.

Action of Hydrogen Chloride and Hydrogen Bromide on Nitrosoalphyls. By EUGEN BAMBERGER, HANS BÜSDORF, and B. SZOLAYSKI (*Ber.*, 1899, **32**, 210—221).—The chief products of the action of hydrogen chloride on nitrosobenzene are paradichlorazoxybenzene, 2 : 4 : 6-trichloraniline, 2 : 4-dichloraniline, parachloraniline, parachlorophenylhydroxylamine, resins, and colouring matters, the reactions taking place being of three kinds.

I. An aldol condensation with the elements of hydrogen chloride to form phenylchlorhydroxylamine which, at the moment of its formation, passes into parachlorophenylhydroxylamine.

II. The further action of the halogen acid on phenylchlorhydroxyl-

amine to form exo-dichloraniline, which instantly passes into the isomeric 2 : 4-dichloraniline.

III. The halogen acid, combining both the properties of the hydrogen and the halogen, acts both as a reducing and a halogenating (that is, oxidising) agent, forming in this way phenylhydroxylamine, which passes into parachloraniline and azoxybenzene, the latter being converted into dichlorazoxybenzene by the further action of the halogen acid.

Hinsberg has shown that alphylsulphinic acids react with nitroso-compounds in the same way as halogen acids, and the fact that the additive product, $OH \cdot NPh \cdot SO_2 \cdot C_7H_7$, is formed when nitrosobenzene is treated with paratolylsulphinic acid is an argument in favour of the intermediate formation of phenylchlorhydroxylamine in the above reactions.

With nitrosotoluene, the reaction is very similar, only in this case the presence of phenols can be detected ; their formation being evidently due to the denitrating action of the mineral acid, $C_6H_4Me \cdot NO + HCl = C_6H_5Me + NOCl$, the latter acting as a diazotising agent, converting a part of the nitrosotoluene into a salt of diazotoluene which yields the cresols and halogenated cresols under the influence of the halogen acid.

The paper concludes with a table giving the comparative weights of the various substances obtained.   J. F. T.

Phenylphosphoric and Phenylenephosphoric Acids. By P. GENVRESSE (*Compt. rend.*, 1898, 127, 522—523).—Phenylphosphoric acid, PO_4H_2Ph (compare Belugou, Abstr., 1898, ii, 558), obtained by heating together phosphoric anhydride and phenol in molecular proportion, forms white crystals, slowly becoming grey, which melt at 89°, are very hygroscopic, and are very soluble in water and alcohol, insoluble in benzene. Belugou's observations on the behaviour of the acid towards indicators are confirmed. Phenylphosphoric acid gives a slightly bluish-white precipitate with a neutral solution of cupric acetate, but is not directly precipitated by ammonium molybdate in nitric acid solution except after previous treatment with potash.

Phenylenediphosphoric acid, $C_6H_4(PO_4H_2)_2$ [$PO_4H_2 : PO_4H_2 = 1 : 4$], obtained by the action of phosphoric anhydride on quinol, forms crystals melting at 168—169° which are very soluble in water, alcohol, and ether, but insoluble in benzene. It is very hygroscopic, is not a reducing agent, gives a greenish precipitate with cupric acetate, is not directly precipitated by ammonium nitromolybdate, and yields quinol on treatment with potash. It behaves like phenylphosphoric acid towards the indicators helianthin and phenolphthalein.

Hydroxyphenylphosphoric acid, $OH \cdot C_6H_4 \cdot PO_4H_2$ [$PO_4H_2 : OH = 1 : 2$], prepared by heating phosphoric anhydride with catechol under diminished pressure and subsequently distilling, crystallises in fine needles melting at 139°; like the preceding compounds, it is very hygroscopic, very soluble in water and alcohol, and insoluble in benzene. It is vigorously attacked by fuming nitric acid, yields a green precipitate with ammonium nitromolybdate, and is decomposed

by potash with the formation of catechol and potassium phosphate. It reduces Fehling's solution after some time, and silver nitrate solution on heating, and is distinguished from other phenols by yielding a red colouring matter when treated with the diazo-derivative of 1 : 4-sulphanilic acid.   N. L.

Isomeric Tribromo-derivatives of Pseudocumenol. By KARL AUWERS (*Ber.*, 1899, **32**, 17—26).—The isomeric tribromo-ψ-cumenol, obtained in the bromination of ψ-cumenol (Abstr., 1896, i, 423 ; 1897, i, 35 ; 1898, i, 647, 648), is now shown to be identical with tribromo-paraxylenol (this vol., i, 35) ; reduction with 2 per cent. sodium amalgam converts it into paraxylenol. The true melting point of tribromoparaxylylic benzoate, which is best prepared by the method of Einhorn and Hollandt (Abstr., 1898, i, 578), is 126—127°. *Para-xylylic phenylcarbamate* (*paraxylenol carbanilate*), $NHPh \cdot COO \cdot C_6H_3Me_2$, obtained by heating paraxylenol with phenylic cyanate in benzene solution for 3 hours at 100°, melts at 160—161° ; the corresponding ψ-*cumylic* and *mesitylic* salts melt at 110—111° and 140—142° respectively.

An isomeric tribromo-ψ-cumenol has, however, been obtained in the following manner. The diacetyl derivative of the compound $C_9H_{10}Br_2O_2$, obtained by heating the nitro-compound from dibromo-ψ-cumenol in glacial acetic acid (this vol., i, 30), is dissolved in acetic acid and gaseous hydrogen bromide is passed in at the ordinary temperature, when a *tribromo-ψ-cumylic acetate*, $OAc \cdot C_6Me_2Br_2 \cdot CH_2Br$, melting at 105—106°, is obtained, which is converted by gaseous hydrogen bromide at a higher temperature into a new *tribromo-ψ-cumenol*,

$$OH \cdot C_6Me_2Br_2 \cdot CH_2Br, \text{ or } C_6HMe_2Br_3 {<}^{CH_2}_{O} \text{ (Abstr., 1898, i, 646)};$$

this melts at 128°, and resembles its isomeride in its properties and reactions, except that the reactions take place more slowly. It is insoluble in alkalis, but is decomposed by them ; one of the bromine atoms is removed under the influence of various reagents ; with boiling methylic alcohol, the *methylic ether*, $OH \cdot C_6Me_2Br_2 \cdot CH_2 \cdot OMe$, melting at 106° and soluble in aqueous alkalis, is formed ; with sodium acetate and acetic acid, the *monacetate*, $OH \cdot C_6Me_2Br_2 \cdot CH_2 \cdot OAc$, melting at 106° and soluble in, but eventually decomposed by, cold alkalis ; with acetone and water, the *phenol-alcohol*, $OH \cdot C_6Me_2Br_2 \cdot CH_2 \cdot OH$, melting at 154—155°. The last substance is better prepared by hydrolysing the diacetyl compound mentioned above with alcoholic potash ; it is reconverted into that compound by boiling with acetic anhydride, and gaseous hydrogen bromide converts it into the tribromo-ψ-cumenol melting at 128°. Possibly these compounds are derivatives of the orthophenol-alcohol, those previously known being para-derivatives.
                                                                       C. F. B.

Action of Nitrous Acid on Resorcinol Monethylic Ether. By CARL KIETAIBL (*Monatsh.*, 1898, **19**, 536—556).—The monethylic ether of resorcinol (metethoxyphenol), in whatever way prepared, is always accompanied by the diethylic ether and unaltered resorcinol ; the best process is to dissolve resorcinol in ether, add sodium ethoxide, and evaporate until the residue has a pasty consistency ; ethylic

iodide is then added, and the whole heated on a water-bath until the alkalinity has disappeared ; the monethylic ether is isolated by acidifying, extracting with ether, and distilling the oil obtained in a current of steam ; the two ethers are thus volatilised and may be separated by means of alkali.

Resorcinol monethylic ether is a thick, pale yellow liquid, sparingly soluble in water, readily in the other common solvents, and distils at 246—247° (uncorr.) under atmospheric pressure ; it darkens rapidly on exposure to air.

When resorcinol monethylic ether (15 grams) is dissolved in a mixture of alcohol (28 grams) and acetic acid (25 grams) and treated cautiously, at a temperature not exceeding $-1°$, with a solution of sodium nitrite (10 grams) in water (20 c.c.), a red substance, a, is soon deposited and may be immediately separated by filtration, whilst from the mother liquor a second crop of crystals, b, is obtained, which may be collected after the lapse of 12 hours ; the mother liquor, on dilution, deposits a third portion, c, of solid matter.

The solid a consists of a mixture of a- and β-orthonitroso- with para-nitroso-resorcinol monethylic ether ; these may be separated by extraction with benzene, which leaves the para-compound undissolved, and on cooling deposits the a-orthonitroso-derivative in a fairly pure state, leaving the β-derivative in solution.

a-*Orthonitrosoresorcinol monethylic ether*, $OEt \cdot C_6H_3(NO) \cdot OH$, is sparingly soluble in water but readily in alcohol, ether, and benzene ; it crystallises from the last-named liquid in golden-yellow, shining needles melting at 133·5° (uncorr.), and gives Liebermann's nitroso-reaction. The *potassium* derivative, $C_8H_8NO_3K$, is sparingly soluble in hot alcohol, and crystallises in slender, olive-green, glistening needles ; when exposed to moisture or air, it becomes red, but reverts to the original tint if heated at 100° ; the *sodium* salt is similar. The aqueous solutions of these salts give a brownish-red precipitate with silver nitrate, and a cherry-red precipitate with mercuric chloride.

a-*Orthamidometethoxyphenol hydrochloride*, $OEt \cdot C_6H_3(OH) \cdot NH_2,HCl$, obtained from the above compound by reduction with stannous chloride and hydrochloric acid, forms colourless prisms which quickly turn violet on exposure to air, and when heated decompose without melting ; its aqueous solution gives a red coloration with ferric chloride.

a-*Orthamidometethoxycarbonylphenol*, $C_7H_4NO_2OEt$, crystallises from benzene in colourless needles, dissolves readily in most of the ordinary solvents, and melts at 150·5—151·5° (uncorr.).

β-*Orthonitrosoresorcinol monethylic ether*, $OEt \cdot C_6H_3(NO) \cdot OH$, dissolves readily in alcohol, benzene, and ether, and crystallises from the last-mentioned liquid in slender needles melting at 102° (uncorr.) ; it gives Liebermann's reaction. The *potassium* and *sodium* derivatives are red ; the *silver* salt, $C_8H_8NO_3Ag$, is a reddish-brown, crystalline precipitate ; on addition of mercuric chloride to the aqueous solution of the sodium salt, a cherry-red precipitate is obtained.

β-*Orthamidometethoxyphenol hydrochloride*, $OEt \cdot C_6H_3(OH) \cdot NH_2,HCl$, crystallises in colourless prisms which quickly become violet coloured on exposure to air ; it is readily soluble in water, alcohol, and dilute

hydrochloric acid, but only sparingly in strong hydrochloric acid ; its aqueous solution gives no coloration with ferric chloride. It differs from the *a*-nitroso-compound in its behaviour towards potash or ammonia, its solution being coloured red on addition of the former, whilst the latter throws down a flocculent, white precipitate, ; the solution of the *a*-derivative, on the other hand, is coloured brown in both cases. *β-Orthamidometethoxycarbonylphenol*, $C_9H_9O_3N$, crystallises in white needles and melts at 125° (uncorr.).

The orthonitrosoresorcinol monethylic ethers have the constitution [OH : NO : OEt = 1 : 2 : 3 and 1 : 6 : 3], but it has not hitherto been possible to decide which of these represents the *a*- and which the *β*-derivative.

Paranitrosoresorcinol monethylic ether, $OEt \cdot C_6H_3(NO) \cdot OH$ [OH : OEt : NO = 1 : 3 : 4], may be purified by crystallisation from absolute alcohol, when it is obtained in pale yellow needles ; it is very sparingly soluble in water, ether, and benzene, but only sparingly so in boiling alcohol. When heated, it darkens at 160—170°, and is completely decomposed below 210°. It gives Liebermann's reaction. This substance appears to be identical with a product obtained by Aronheim (Abstr., 1878, 465) and by Kraus (Abstr., 1892, 44) from the product of interaction of nitrous acid and resorcinol diethylic ether. The *sodium* salt is a greyish-green, crystalline substance, which, on exposure to air, becomes lighter in tint, but at 100° resumes its original colour. The aqueous solution of the sodium salt gives, with silver nitrate, an orange-yellow, and with mercuric chloride, a cherry-red precipitate.

Paramidometethoxyphenol hydrochloride, $OEt \cdot C_6H_3(OH) \cdot NH_2, HCl$, crystallises in large, colourless needles, which become violet on exposure to the air, and when heated decompose without melting. Ferric chloride produces a violet coloration in its aqueous solution. The crystals belong to the rhombic system, the axial ratio being approximately $a : b : c = 0.8616 : 1 : 0.5899$. It does not give a carbonyl derivative when heated with carbamide, and when oxidised with sodium chromate yields ethoxyquinone.

A fourth substance may be isolated from *b* and *c* ; this melts at 176°, dissolves sparingly in boiling water, more readily in alcohol, ether, and ethylic acetate, and crystallises from hot alcohol in silky, greenish-yellow needles ; it gives Liebermann's reaction. Its composition is nearly expressed by the formulæ $C_{16}H_{18}N_2O_5$ or $C_{16}H_{20}N_2O_5$, which are not, however, in agreement with its observed molecular weight (170—190) as determined in melted phenol or boiling ether, or with the analysis of a hydrochloride which is produced on reducing it with stannous chloride. It is possible, therefore, that the substance is not homogeneous.   A. L.

Mesityl Oxide and Ethylic Malonate. By DANIEL VORLÄNDER (*Ber.*, 1899, **32**, 245. Compare Crossley, Proc., 1899, **15**, 52).—The condensation products recently described by Crossley (Proc., 1898, **14**, 247) have already been examined by Vorländer (Abstr., 1897, i, 275, 276) and have been shown to be derivatives of dihydroresorcinol ; the oxidation products have also been examined (this vol., i, 259).

T. M. L.

Derivatives of Catechol. By H. Cousin (*Ann. Chim. Phys.*, 1898, [vii], 480—533. Compare Abstr., 1892, 1443; 1893, i, 258, 637; 1894, i, 368; 1895 i, 456).—A detailed account of work already published.   G. T. M.

Separation of the Dimethylic Ethers of Pyrogallol and of Methylpyrogallol. By OTTO ROSAUER (*Monatsh.*, 1898, 19, 557—570).—Commercial pyrogallol dimethylic ether, as supplied by Schuchardt, is a somewhat complex mixture. In order to effect the separation of the constituents, it was distilled, and the two fractions boiling at 250—260° and 260—270° treated separately. The portion of lower boiling point was treated, in benzene solution, with sodium and ethylic chloroformate, the liquid separated by filtration from sodium chloride, and then evaporated; the crystals which were deposited were separated by fractional distillation into a portion boiling at 183° under 50 mm. pressure, and another portion boiling at 191° under 20 mm. pressure.

Pyrogallol dimethylic ether ethylic carbonate, $COOEt \cdot O \cdot C_6H_3(OMe)_2$, the crystalline constituent boiling at 183° under 50 mm. pressure, is deposited from methylic alcohol in colourless, prismatic crystals, melts at 63—65°, is volatile in steam, and dissolves very readily in the ordinary solvents, with the exception of light petroleum. When boiled with baryta water, it is decomposed, forming pyrogallol dimethyl ether, which yields pyrogallol when heated with hydriodic acid.

The portion boiling at 191° under 20 mm. pressure, is *methylpyrogallol dimethylic ether ethylic carbonate*, $COOEt \cdot O \cdot C_6H_2Me(OMe)_2$; it crystallises from alcohol in short, colourless, prismatic needles melting at 111—113°. It is nearly insoluble in boiling water, and is only sparingly soluble in light petroleum, but dissolves readily in ether, benzene, and hot alcohol, and is volatile in steam. Methylpyrogallol dimethylic ether, $C_6H_2Me(OMe)_2 \cdot OH$, produced when the foregoing substance is boiled with baryta water, melts at 29—30°, boils at 145—146° under 12 mm. pressure, and dissolves somewhat readily in water and in the usual solvents; ferric chloride imparts a violet colour to the aqueous solution. Methylpyrogallol crystallises from benzene in slender, colourless, felted needles, and melts at 116—119°; its aqueous solution is coloured bluish-violet by ferric chloride, whilst, with alkalis, it gives a bright yellowish-red, which slowly becomes dark brownish-red. With ferrous sulphate, it behaves like pyrogallol and when fused with potash it yields gallic acid. The author concludes that methylpyrogallol dimethylic ether is identical with that obtained by Hofmann, and therefore has the constitution $Me:OH:(OMe)_2 = 1:3:5:4$. *Methylpyrogallol triacetate*, $C_6H_2Me(OAc)_3$, prepared by heating methylpyrogallol with acetic anhydride at 134°, crystallises from a mixture of benzene and petroleum in yellowish tablets, which, perhaps, belong to the triclinic system, the axial ratio being $a:b:c = 1\cdot19:1:1\cdot54$, $ac = 90° \ 44'$.   A. L.

Nitration of Guaiacol. By GUSTAV KOMPPA (*Chem. Centr.*, 1898, ii, 1169; from *Oefversigt af Finska Vet.-Soc. Förhandlingar*, 40).—When an ice-cold solution of guaiacol in glacial acetic acid is treated with an ice-cold mixture of 1 volume of fuming nitric acid with 4

volumes of glacial acetic acid, water then added, and the liquid distilled with steam, yellow crystals which melt at 65° and are, perhaps, mono-nitroguaiacol, separate from the distillate. The non-volatile residue yields Herzig's dinitroguaiacol (Abstr., 1883, 464). The *acetyl* derivative, $OMe \cdot C_6H_2(NO_2)_2 \cdot OAc$, crystallises in yellowish plates, and melts at 114°; it is rather easily soluble in hot, but only slightly so in cold, alcohol, and is insoluble in water. E. W. W.

Synthesis of Asarone. By LUDWIG GATTERMANN and F. EGGERS (*Ber.*, 1899, **32**, 289—291).—When 1 : 2 : 4-trimethoxybenzene is acted on by hydrogen cyanide in presence of hydrogen chloride and aluminium chloride (compare Abstr., 1898, i, 476 and 581), it is converted into 1 : 2 : 4 : 5-trimethoxybenzaldehyde ; the identity of this with asarylic aldehyde obtained from asarone by oxidation is shown by its melting point, by the properties of its azine, and by its yielding asaronic acid when oxidised with potassium permanganate. When the aldehyde (2 grams) is heated with propionic anhydride (3 grams) and sodium propionate (1 gram) during 7 hours at 150°, it is converted, to the extent of 60 per cent., into asarone ; the latter is therefore shown to be 1 : 2 : 4 : 5-trimethoxypropenylbenzene, $CH_3 \cdot CH \colon CH \cdot C_6H_2(OMe)_3$. The view that the aldehyde from which it was obtained contains the CHO-group in position 5 is justified by its method of preparation, which, according to all analogous instances (*loc. cit.*), necessitates this group being in the para-position relatively to the methoxyl. Together with asarone, there is formed in the above synthesis a small quantity of *trimethoxy-α-methylcinnamic acid*, $C_6H_2(OMe)_3 \cdot CH \colon CMe \cdot COOH$, as an intermediate product ; this separates from alcohol in stout, colourless crystals, and melts at 157°. W. A. D.

Oxidation Products of Diquinoyltetroxime. By RUDOLPH NIETZKI and W. GEESE (*Ber.*, 1899, **32**, 505—507).—1 : 2 : 3 : 4-*Tetra-nitrosobenzene*, $C_6H_2(NO)_4$, prepared by adding sodium hypochlorite to a solution of diquinoyltetroxime in concentrated sodium carbonate, crystallises from alcohol in colourless needles, and melts at 93°; reduction with stannous chloride converts it into tetramidobenzene.

Nitrotetranitrosobenzene, $NO_2 \cdot C_6H(NO)_4$, obtained by the action of fuming nitric acid, crystallises from alcohol or from acetic acid in yellow needles, and melts at 158°.

2 : 3-*Dinitrosoquinoneoxime*, $C_6H_2(NO)_2(NOH)_2$, produced on oxidising diquinoyltetroxime with nitric acid, crystallises from alcohol in needles, and melts at 68°. M. O. F.

Oxidation of Aromatic Compounds. By WILLIAM ŒCHSNER DE CONINCK and A. COMBE (*Compt. rend.*, 1899, **128**, 239—240).— When orthamidophenol, paramidophenol, the three amidobenzoic acids, ortho- and para-nitrophenol, paranitrotoluene, picric acid, benz-amide, salicylamide, and hydrobenzamide are oxidised with chromic mixture, no nitrogen is liberated. Picramic acid, on the other hand, yields a small quantity of nitrogen as well as carbonic anhydride. C. H. B.

Oxidation of Aromatic Bases. By EUGEN BAMBERGER and FRED. TSCHIRNER (*Ber.*, 1899, **32**, 342—355).—When aniline, in

sulphuric acid solution, is oxidised with potassium permanganate in presence of a small quantity of formaldehyde, it gives rise to nitrobenzene, azoxybenzene, and paradiamidodiphenylmethane, in addition to nitrosobenzene, which is the principal product (Abstr., 1898, i, 518). Phenylhydroxylamine is probably formed initially, but cannot be isolated owing to the ease with which it is oxidised to nitrosobenzene. From the experiments which follow, the authors conclude that the first step in the oxidation is the formation of the additive compound, $C_6H_5 \cdot NH_2 : O$, which immediately undergoes isomeric change to form phenylhydroxylamine.

Aqueous hydrogen peroxide acts only very slowly on dimethylaniline in the cold; when, however, the base (50 grams) is strongly agitated with the oxidising agent (1410 c.c. of a 3·2 per cent. solution) for 12 hours at 60—70°, it is almost completely converted into *dimethylaniline oxide*, $NPhMe_2 : O$, which can be precipitated as the *picrate*, $NPhMe_2O, C_6H_3N_3O_7$; this crystallises in sulphur-yellow, monosymmetric needles having a silky lustre, melts at 137—138°, and decomposes at a slightly higher temperature; it is converted by warm, concentrated hydrochloric acid into the *hydrochloride*, $C_8H_{11}NO, HCl$, which forms transparent, lustrous, deliquescent prisms, melts and decomposes at 124—125°, and when treated with moist silver oxide, gives rise to the *base*, $C_8H_{11}O$. This crystallises in beautiful, colourless, deliquescent prisms, has a bitter taste, softens at about 146°, melts at 152—153°, and is decomposed at a slightly higher temperature with the production of dimethylaniline, which is also obtained when hydrogen sulphide is passed through an aqueous solution of the oxide, or when the latter is reduced with zinc and hydrochloric acid. Unlike triethylamine oxide, $NEt_3 : O$ (Bewad, Abstr., 1889, 112), dimethylaniline oxide has no reducing properties, and is stable in presence of dilute alkalis, whilst it differs from the alkylpiperidine oxides (Merlin, Abstr., 1893, i, 113; Wernick and Wolffenstein, Abstr., 1898, i, 536) in not liberating iodine from potassium iodide. The *platinochloride*, $(C_8H_{11}NO)_2, H_2PtCl_6 + nH_2O$, crystallises from water in orange-red, lustrous, rhombic plates, and melts, after being dried in a vacuum over sulphuric acid, indefinitely at 136—137°, and decomposes at 146°; the *aurichloride*, $C_8H_{11}NO, HAuCl_4$, forms lustrous, yellow needles, and is somewhat sparingly soluble in water, whilst the *ferrocyanide*, $(C_8H_{11}NO)_2, H_2FeC_6N_6$, is a white, crystalline powder, which, when heated, explodes at 144·5°. When dimethylaniline oxide is acted on by nitrous acid, it gives rise principally to ortho- and para-nitrodimethylaniline; this is explained by assuming that nitrosodimethylaniline oxide, $NO \cdot C_6H_4 \cdot NMe_2 : O$, is first formed, and then undergoes isomeric change. When the hydrochloride of the base is warmed on the water-bath for several hours with an excess of benzaldehyde, malachite-green is formed without it being necessary to employ a dehydrating agent.

Diethylaniline oxide, $NPhEt_2 : O$, is formed, together with formic acid and other substances, by the action of hydrogen peroxide on diethylaniline; the *picrate*, $C_{16}H_{18}N_4O_8$, separates from alcohol in dark yellow prisms resembling salt crystals. The *picrates*, $C_{15}H_{16}N_4O_8$, of dimethylortho- and dimethylpara-toluidine oxides crystallise in

yellow needles, and melt at 145·5—146·5° and 106—107° respectively.　　　　　　　　　　　　　　　　　　　　　　　　W. A. D.

Action of Alcoholic Hydrogen Chloride on Nitrosophenylglycine [Nitrosoanilidoacetic Acid]. By OTTO FISCHER (*Ber.*, 1899, **32**, 247—249. Compare Abstr., 1887, 1115).—When nitrosoanilidoacetic acid is boiled with water, it is decomposed into carbonic anhydride and nitrosomethylaniline; the alkali salts, however, are stable. The *ammonium* salt crystallises in pearly flakes and dissolves readily in water; the *phenylhydrazine* salt separates from alcohol, in which it is only slightly soluble, in beautiful, white flakes, and melts at 124°; the *ethylic* salt is a brownish-yellow oil.

By the action of alcoholic hydrogen chloride on nitrosoanilidoacetic acid or its ethylic salt, an explosive substance is produced which is regarded as the chloride of paradiazophenylhydroxylamine, $OH \cdot NH \cdot C_6H_4 \cdot N_2Cl$ (Fischer and Hepp, *loc. cit.*). The *aurichloride*, $C_6H_5N_3O,HAuCl_4$, which crystallises in reddish needles, is decomposed by cold water, but not by concentrated hydrochloric acid. The *sulphate* forms yellow needles and is somewhat more stable. The addition of phenylhydrazine to the dry chloride causes it to explode, whilst in concentrated alcoholic or ethereal solution there is a vigorous evolution of nitrogen; in dilute solution, the hydrochloride of phenylhydrazine is slowly deposited. Diazophenylhydroxylamine has not been converted either into phenylhydroxylamine or into nitrosobenzene, but by warming its alcoholic solution or by acting on it with copper powder, nitrogen is evolved and azoxybenzene produced.　　　　　　　　　　　　　　　　　　　　　　　　T. M. L.

Maleic Derivatives of some Aromatic Amines. By ERCOLE GIUSTINIANI (*Gazzetta*, 1898, **28**, ii, 189—192).—The author proposes extending the method employed by Giustiniani and Piutti for preparing maleic derivatives of fatty monamines and of benzylamine to other aromatic amines with a view of finding a good method for preparing substituted maleimides.　　　　　　　　　　　　T. H. P.

Orthobromoparanisidine. By ALBERTO BENEVENTO (*Gazzetta*, 1898, **28**, ii, 202—208).—Staedel prepared orthobromoparanisidine by reducing orthobromoparanitranisoil and described it as an oil. The author has obtained it crystalline by the following method: paranisidine and succinic acid, heated together, give paramethoxyphenylsuccinimide, the orthobromo-derivative of which, on treatment with hydrochloric acid, yields acicular crystals of the hydrochloride of orthobromoparanisidine. The base forms yellowish crystals melting at 60—61°; it is soluble in hot water, ether, alcohol, and ethylic acetate, and is stable to light. The *sulphate*, *oxalate*, and *succinate* were prepared, the last named forming acicular crystals melting at 61°.　　　　　　　　　　　　　　　　　　　　　　　　T. H. P.
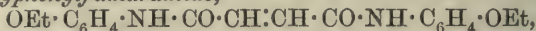
Action of Malic Acid on Paramidophenetoil. By G. CAMPANARO (*Gazzetta*, 1898, **28**, ii, 192—197).—Amidophenetoil *hydrogen malate*, $NH_2 \cdot C_6H_4 \cdot OEt,COOH \cdot C_2H_3(OH) \cdot COOH$, is readily obtained by the combination of malic acid and paramidophenetoil, and separates from hot water in white crystals melting at 150°; on heating, it

loses a molecule of water, forming *parethoxyphenylmalamic acid*, OEt·C$_6$H$_4$·NH·CO·C$_2$H$_3$(OH)·COOH, which, when purified by crystallisation from hot water, is obtained in small, yellowish needles melting at 160°, and is very soluble in hot water, alcohol, and ether. The *silver* salt, C$_{12}$H$_{14}$AgNO$_5$, was prepared, and the *barium* salt, (C$_{12}$H$_{14}$NO$_5$)$_2$Ba, forms splendid, white, acicular crystals. The *ethylic* salt, C$_{12}$H$_{14}$EtNO$_5$, is crystalline and melts at 235°; it is very soluble in water, less so in alcohol and ether.

Acetylethoxyphenylmalamic acid, obtained by the action of acetic anhydride on ethoxyphenylmalamic acid, crystallises in lustrous, white needles melting at 140°, and is slightly soluble in hot water.

Parethoxyphenylfumaramide,
OEt·C$_6$H$_4$·NH·CO·CH:CH·CO·NH·C$_6$H$_4$·OEt,
obtained by heating malic acid with paraphenetidine at 180°, or by heating parethoxyphenylmalamic acid, forms shining, yellowish leaves melting at 214°. It readily takes up bromine, giving *parethoxyphenylbromosuccinamide*, OEt·C$_6$H$_4$·NH·CO·CHBr·CHBr·CO·NH·C$_6$H$_4$·OEt, which forms whitish crystals melting at 199°.   T. H. P.

Ortho-substituted Alkylanilines. By PAUL FRIEDLÄNDER (*Monatsh.*, 1898, **19**, 627—646).—The author has found that all ortho-substituted dialkylanilines (not substituted in the para-position) do not react with nitrous acid or with aldehydes. The power of combining with diazo-compounds is also greatly diminished, but not completely lost. These bases, moreover, invariably boil at lower temperatures than the corresponding monalkyl derivatives, whereas other dialkylanilines boil at higher temperatures than the corresponding monomethyl compounds. The two diortho-substituted dialkylanilines examined also behaved similarly. Ethylorthotoluidine boils at 214° (corr.), and condenses with formaldehyde, producing *diethyldiamidodiorthotolylmethane*, which crystallises in yellowish needles, melts at 96°, and boils at about 300° under a pressure of 40 mm. Ethylic iodide converts it into the corresponding *tetrethyl* compound, which is a yellow oil boiling at 235—245° under 26 mm. pressure. Diethylorthotoluidine does not react with formaldehyde. *Ethylorthophenetidine* is a colourless oil which boils at 238°, and readily reacts with formaldehyde and diazo-compounds. *Diethylorthophenetidine* boils at 231—233°, and forms a *platinochloride* which crystallises in light yellow needles. It does not react with nitrous acid or formaldehyde, but forms a red azo-colouring matter with paranitrodiazobenzene. Monomethylorthonitraniline, which can be prepared by methylating orthonitraniline, yields a condensation product with formaldehyde. *Dimethylorthonitraniline* is best prepared by heating crude orthodinitrobenzene with dimethylamine. It is a reddish-yellow oil which decomposes when heated, and does not react with nitrous acid, aldehydes, or diazo-compounds; the *platinochloride* crystallises in short, yellow needles. Orthamidobenzonitrile melts, when pure, at 50—51°, and its *acetyl* derivative at 132·5°. *Ethylorthamidobenzonitrile* crystallises in long, colourless needles melting at 32°, and yields azo-colouring matters in the usual manner; its *acetyl* derivative is liquid, and boils at 268—275°. *Diethylorthamidobenzonitrile* boils

at 165—175° under 95 mm. pressure, and does not react with nitrous acid or diazo-compounds. Dimethylorthochloraniline, when pure, does not react with nitrous acid as stated by Heidlberg (Abstr., 1887, 474); it boils at 206°, whilst the monomethyl compound boils at 214°.

DERIVATIVES OF METAXYLIDINE [$Me_2 : NH_2 = 1 : 3 : 2$]. [With PH. BRAND.]—The *benzoyl* derivative crystallises in silky needles melting at 164°. Metaxylidine very readily reacts with formaldehyde, yielding *diamidodixylylmethane*, $CH_2(C_6H_2Me_2 \cdot NH_2)_2$, which crystallises in white needles melting at 126°, and forms a *diacetate* crystallising in plates which do not melt below 280°. It also reacts with para-nitrobenzaldehyde, forming *paranitrodiamidophenyldixylylmethane*, $NO_2 \cdot C_6H_4 \cdot CH(C_6H_2Me_2 \cdot NH_2)_2$, which melts at 136°, and yields a *diacetyl* compound crystallising in colourless needles. Metaxylidine readily forms a dark red azo-colouring matter with para-nitrodiazobenzene. *Methylmetaxylidine*, formed by the action of methylic iodide on the base, is a colourless oil boiling at 206—207°; the *hydrochloride* is readily soluble, and the *platinochloride* forms yellow needles. Its *acetyl* derivative crystallises in large tablets and melts at 94—95°; all attempts to hydrolyse this compound were unsuccessful, as it resists the action of boiling 80 per cent. sulphuric acid, or of alcoholic potash at 220°. Condensation products with aldehydes or azo-colouring matters could not be obtained from the base, and this diortho-substituted monomethylaniline therefore behaves in this respect like a monortho-substituted dimethylaniline. *Dimethylmetaxylidine* boils at 195—196°, and smells like camphor; it does not react with nitrous acid, aldehydes, or diazo-compounds. *Ethylmetaxylidine* is a colourless oil boiling at 217—218°, and closely resembles the corresponding methyl compound. The *diethyl* derivative boils at 220—221°, and forms a *platinochloride* crystallising in small, yellow needles. A. H.

The Quinquevalent Asymmetric Nitrogen Atom. I. Occupation of Space. II. Inactive Isomerides. By EDGAR WEDEKIND (*Ber.*, 1899, **32**, 511—516, 517—529).—The author has endeavoured to ascertain the capacity of nitrogen compounds for yielding derivatives in which the nitrogen is quinquevalent. The possible formation of inactive isomerides has also been kept in view, and the question of optical activity arising from asymmetry of nitrogen has been considered.

When diphenylmethylamine is heated with methylic iodide (1 mol.) during 5—6 hours at 150°, no substituted ammonium iodide is produced, although a mixture of dimethylaniline and methylic iodide yields 93 per cent. after an interval of 53 hours without application of heat; dimethylaniline yields only 3 per cent. of the ammonium iodide when treated with cold normal propylic iodide, and 0·9 per cent. with isopropylic iodide, whilst allylic iodide gives 88·5 per cent. Methylic iodide has no action on cold di-isopropylaniline, with which action does not begin until a temperature of 100° is reached.

Isopropylic iodide yields 4 per cent. of ammonium salt when heated with tribenzylamine at 100° during 6 hours, whilst the normal iodide has no action. This peculiarity must depend less on the pentad nature of

nitrogen than on the influence of the benzylic radicle, because dimethylaniline under similar conditions combines less readily with isopropylic iodide than with the normal salt. In this connection, it is noteworthy that when benzylic chloride acts on allylaniline, a considerable amount of dibenzylaniline is produced ; the latter is also formed when allylic bromide acts on benzylaniline.

Attempts to produce the same system by introducing the radicles in different order have been shown to meet with various degrees of success (compare Menschutkin, Abstr., 1895, ii, 385). It should be possible to prepare phenylbenzylethylallylammonium iodide by the three following methods. 1. Action of benzylic iodide on ethylallylaniline. 2. Action of allylic iodide on benzylethylaniline. 3. Action of ethylic iodide on benzylallylaniline. In practice, however, the first only of these methods was successful, whilst the third produced no result whatever.

Acetomethylanilide does not combine with methylic iodide when heated at 150° during 5 hours, but yields a viscous oil at 220—250° ; this illustrates the influence exerted by negative radicles on the ease with which substituted ammonium salts are produced. Compounds more strongly basic in character do not display this feature to the same extent, *ethylic piperidinoacetate benzyl-bromide* or *-iodide* being formed when ethylic bromacetate or iodacetate acts on benzylpiperidine ; the iodide, $C_5H_{10}NI(CH_2Ph)\cdot CH_2\cdot COOEt$, crystallises in monoclinic plates or prisms, and melts at 193—195°. Methylic bromacetate and iodacetate combine very readily with benzylpiperidine, which also yields an ammonium salt with methylic bromomalonate ; the products in each case, excepting the last, can be prepared by the inverse process, namely, addition of benzylic iodide or bromide to the ethereal piperidinoacetate, $C_5H_{10}N\cdot CH_2\cdot COOR$. These ammonium iodides lose a portion of their halogen on treatment with a boiling solution of barium hydroxide, the ethereal carboxylate being simultaneously hydrolysed.

In certain circumstances, therefore, two affinities of quinquevalent nitrogen can be satisfied by negative radicles. This has been shown by Lachmann, who prepared triethylamine dibromide, NEt_3Br_2, but failed to obtain nitrogen pentethyl, NEt_5, from it by the action of zinc ethyl ; moreover, molecular silver has no action on phenyltrimethylammonium bromide.

Phenylparanitrobenzyldimethylammonium chloride,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot NMe_2PhCl,$$

obtained from paranitrobenzylic chloride and dimethylaniline, crystallises from a mixture of ether and alcohol in colourless leaflets, and melts at 118—120°.

It has been noticed by Le Bel that trimethylisobutylammonium platinochloride occurs in two forms which differ crystallographically from one another, and observations of a similar character have been made by Collie and Schryver, Menschutkin, and Miss Evans ; the author finds that phenylbenzylmethylallylammonium iodide, when prepared by the addition of allylic or benzylic iodide to benzylmethylaniline or methylallylaniline respectively, differs in physical properties from the salt obtained by the action of methylic iodide on benzylallylaniline.

α-Phenylbenzylmethylallylammonium iodide, $CH_2Ph \cdot NMe(C_3H_5)PhI$, prepared by agitating benzylmethylaniline (20 grams) with allylic iodide (17 grams), and filtering the crystalline product after an interval of 24 hours, crystallises from 50 per cent. alcohol, and melts and decomposes at 140—142°; it is identical with the product from methylallylaniline and benzylic iodide. The salt crystallises in the rhombic system [$a : b : c = 0.8915 : 1 : 0.6637$]. The *β-modification*, obtained by the action of methylic iodide (13.6 grams) on benzylallylaniline (17.6 grams) during 3—4 days, crystallises from 50 per cent. alcohol in beautiful prisms belonging to the rhombic system [$a : b : c = 0.6779 : 1 : 1.0392$], and melts at 158—159°. The specific gravity is higher than that of the isomeride.

Benzylallylaniline, $C_3H_5 \cdot NPh \cdot CH_2Ph$, prepared from allylaniline and benzylic chloride, boils at 215—225° under 42 mm. pressure ; the *hydrochloride* crystallises from alcohol in colourless leaflets and melts at 220—221°. The *methylallylaniline*, $NMePh \cdot C_3H_5$, obtained from allylic bromide and methylaniline, boils at 213° under a pressure of 755 mm.

The author has examined numerous ammonium iodides, which will be described in a subsequent communication ; several cases of isomerism similar to that exhibited by the phenylbenzylmethylallylammonium iodides have been observed. M. O. F.

Action of Formaldehyde on Orthodiamines II. By OTTO FISCHER (*Ber.*, 1899, **32**, 245—247).—Fischer and Wreszinski (Abstr., 1892, 1496) have previously shown that, by the action of formaldehyde on orthodiamines in acid solution, methylated imidazoles are produced, whilst in neutral solution more complex bases are formed by the condensation of two molecules of the diamine with four molecules of formaldehyde. The base from orthophenylenediamine has the composition $C_{16}H_{16}N_4$, and the formula $C_6H_4 \left\langle \begin{matrix} N \\ N \end{matrix} \right\rangle \begin{matrix} CH_2 \\ CH_2 \end{matrix} \begin{matrix} CH_2 \\ CH_2 \end{matrix} \left\langle \begin{matrix} N \\ N \end{matrix} \right\rangle C_6H_4$ is now assigned to it. The salts gradually undergo decomposition when exposed to the air, yielding formaldehyde, and a similar decomposition takes place on boiling with dilute sulphuric acid ; in the latter case, the original diamine can be detected amongst the products. In accordance with the formula assigned to it, the base is very stable towards reducing agents, and when dissolved in alcohol or amyl alcohol it is not acted on either by sodium or by potassium ; towards alkylic iodides, it behaves as a tertiary base, and combines directly with two molecular proportions of methylic or ethylic iodide. A similar formula has recently been assigned by Bischoff (this vol., i, 279) to the analogous base prepared from formaldehyde and ethylenediamine.

T. M. L.

Phenylparatolylformamidine and the Transformation of Imidoethers. By HENRY L. WHEELER and T. B. JOHNSON (*Ber.*, 1899, **32**, 35—41. Compare Abstr., 1897, i, 465).—After examining Walther's results experimentally (Abstr., 1898, i, 519 ; 1897, i, 242), the authors arrived at the following conclusions. " Up to the present, only one phenylparatolylformamidine is known. It melts at 86° when

pure. This amidine is the only mixed amidine that is formed in all four of Zwingenberger and Walther's experiments, but its detection is rendered difficult by the presence of other amidines; these are diphenylamidine and diparatolylamidine. The supposed phenyl-paratolylamidine melting at 132° is nothing but impure diparatolyl-amidine, that melting at 120° is impure diphenylamidine, whilst those melting at 102° and 98° are mixtures of phenylparatolylamidine, diphenylamidine, and diparatolylamidine in varying proportions."

When the silver derivative of formanilide, NPh:CH·OAg, is heated with excess of ethylic iodide at 100° for 6 hours, the product is not phenylformimidoethylic ether, NPh:CH·OEt, but formethylanilide NEtPh·CHO. In a similar manner, benzimido-ethylic ether, NH:CPh·OEt, yields benzethylamide, NHEt·CPhO. C. F. B.

A New Class of Dyes, the Diamidodiphenylbenzenyl-amidines. By EMILIO NOELTING and KUNTZ (*Chem. Centr.*, 1898, ii, 1049; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 395—397).—Diphenyl-benzenylamidine, NPh:CPh·NHPh, and its methyl derivative are white, and have no colouring properties, but when an amido- or a dimethylamido-group is introduced into these compounds, faint yellow dyes are formed, and by the introduction of two such groups diamido-diphenylbenzenylamidines are obtained which dye wool, silk, and cotton mordanted with tannin, an intense yellow. The latter dyes are prepared by the action of dimethylparamidobenzomethylanilide on aniline, paraphenylenediamine, or dimethylparaphenylenediamine in presence of phosphorus oxychloride. Diphenylbenzenylmethyl-amidine must therefore be regarded as a chromogen, since it yields dyes when auxochromic groups are introduced into it.

E. W. W.

Amidines (Iminoamines). By FERNAND MUTTELET (*Ann. Chim. Phys.*, 1898, [vii], 14, 391—432).—A study of the reaction between aromatic mono-substituted orthodiamines and benzoic chloride and its derivatives (Abstr., 1898, i, 412). When 2-amidodiphenylamine is heated at 215° with excess of 4-nitrobenzoic chloride, the inner *anhydride*, $C_6H_4\diagdown\!\!\!\!\!\!^{NPh}_{-N}\!\!\!\!\!\!\diagup C·C_6H_4·NO_2$, is produced; it crystallises from alcohol in needles melting at 174°. The *anhydride* obtained in a similar manner from 2-amidophenylparatoluidine, crystallises in yellow needles melting at 174—175°.

The *anhydride*, $NO_2·C_6H_3\diagdown\!\!\!\!\!\!^{NPh}_{-N}\!\!\!\!\!\!\diagup C·C_6H_4·NO_2$, obtained from 4-nitro-2-amidodiphenylamine and 4-nitrobenzoic chloride, crystallises from benzene in yellow, lamellated crystals melting at 205°.

The *anhydride* containing the paratolyl group in the place of phenyl in the preceding compound, crystallises from benzene in yellow scales and melts at 250—251°.

These nitro-anhydrides, on reduction, yield amido-amidines (compare *loc. cit.*); the following are described for the first time. The *compound* $C_6H_4\diagdown\!\!\!\!\!\!^{NPh}_{-N}\!\!\!\!\!\!\diagup C·C_6H_4·NH_2$ melts at 198—199°; its *sulphate* crystallises with $2H_2O$, and its *hydrochloride* with $1\frac{1}{2}H_2O$. The corre-

sponding *paratolyl* compound melts at 187—188°; its *sulphate* and *hydrochloride* are described. The *compound* $NH_2 \cdot C_6H_4 <^{NPh}_{-\cdot N} > C \cdot C_6H_4 \cdot NH_2$ crystallises in needles and melts at 270—272°, its *sulphate* crystallises with $1\frac{1}{2}H_2O$; the *paratolyl* compound melts at 252—253°; its *sulphate* crystallises with $4H_2O$.

The amidines containing one amido-group, just described, yield azo-derivatives when diazotised and combined with β-naphthol; the amidines containing two amido-groups give rise to tetrazo-compounds. The azo-dyes obtained from the monamidoamidines and naphthol- and amidonaphthol-sulphonic acids are incapable of dyeing unmordanted cotton, whereas the tetrazo-compounds from the diamidoamidines are substantive colours comparable with those of commerce.

G. T. M.

Hydrolysis of Mixed Azo-compounds. By EUGEN BAMBERGER (*Chem. Centr.*, 1898, ii, 1050; from *Arch. Sci. phys. nat. Genève*, [iv], **6**, 384—385).—The relationship of alphylazonitroparaffins to phenylhydrazine is shown by their decomposition into nitrous acid and β-acylphenylhydrazides by the action of alkalis. Phenylazonitropropane yields propionophenylhydrazide, $EtCO \cdot N_2H_2Ph$; phenylazonitroethane yields acetophenylhydrazide, and phenylazonitropentane gives valerophenylhydrazide. In a similar manner, oxyformazyl is formed from nitroformazyl, but cannot be isolated, as it changes into the betaine of diphenyloxytetrazolium hydroxide, $N <^{NPh \cdot NPh}_{C = N} > O |$, which crystallises in white needles, explodes at 174°, and yields insoluble salts with potassium permanganate, potassium dichromate, picric acid, and gold and platinum chlorides.

E. W. W.

Ethylic [*b*-**Aniline-azo**] -**acetoacetate (Ethylic Acetylglyoxylate-α-phenylhydrazone, Ethylic Benzeneazoacetoacetate).** By CARL BÜLOW (*Ber.*, 1899, **32**, 197—210. Compare this vol., i, 271). —The compound formed when the sodium compound of isodiazobenzene reacts with ethylic acetoacetate in slightly alkaline solution, is identical with that obtained by Kjellin from this ethylic salt and benzenediazonium chloride, and is evidently *ethylic benzeneazoacetoacetate*, $Ph \cdot N_2 \cdot CHAc \cdot COOEt$; it crystallises in broad, sulphur-yellow needles, melts at 73—74°, and dissolves in 1 per cent. sodium hydroxide solution with an intense red coloration, the solution being decomposed by carbonic anhydride, with re-formation of the ethylic salt. It would therefore seem that the CH-group, in conjunction with the chromophore group N:N, acts as an auxochrome.

Sodium benzeneazoacetoacetate, prepared by adding sodium hydroxide solution to an alcoholic solution of the ethylic salt, forms yellowish-white crystals, melts at 195°, and, on further treatment with sodium hydroxide, forms a disodium compound, which is, however, stable only in dilute alkaline solution; the sodium salt is not decomposed by carbonic anhydride. The phenylhydrazone of the acid is best prepared by adding an alcoholic solution of phenylhydrazine to an aqueous solution of the sodium salt; it can be precipitated, not only

by the addition of acetic acid, but also by means of mineral acids, without being converted into 1-phenyl-3-methyl-4-benzeneazo-5-pyrazolone, which is formed only on boiling the solution. The *methylamide*, which is prepared by adding methylamine to an alcoholic solution of the ethylic salt, crystallises in yellow needles melting at 150·5°, and on nitration passes into paranitrobenzeneazoacetoacetomethylamide melting at 190°.

Ethylic benzeneazoacetoacetate-β-phenylhydrazone is very unstable, readily passing into the pyrazolone by the elimination of alcohol; it forms orange needles and melts at 108—109°.

On nitration, ethylic benzeneazoacetoacetate gives the same nitro-compound as that prepared from the isodiazo-derivative of paranitraniline and ethylic acetoacetate; this, on treatment with phenylhydrazine, passes into 1-phenyl-3-methyl-4-benzeneazo-5-pyrazolone, melting at 198°; the true *β-phenylhydrazone*, prepared from the sodium salt of the acid by the addition of phenylhydrazine, is an orange, crystalline powder which readily passes into the pyrazolone on heating with acids.   J. F. T.

Unsymmetrical Phenylhydrazine Derivatives. V. Ethylic Phenylhydrazidoformate. By HANS RUPE and HANS LABHARDT (*Ber.*, 1899, **32**, 10—17. Compare Abstr., 1896, i, 429).—*Ethylic acetophenylhydrazidoformate*, $NHAc\cdot NPh\cdot COOEt$, is obtained by boiling acetophenylhydrazide (1 mol.) with ethylic chloroformate (1 mol.) in benzene solution; it melts at 72—73°. When it is distilled, it loses alcohol and yields 1-phenyl-4-methyl-3-oxybiazolone, $\begin{matrix} NPh\cdot CO \\ | \quad\quad\quad\; \\ N{=}CMe \end{matrix}\!\!>\!O$

(Freund and Goldschmidt, Abstr., 1888, 686, 1187); when boiled with 10 per cent. sulphuric acid and enough alcohol to effect solution, it is converted into ethylic phenylhydrazidoformate, $NH_2\cdot NPh\cdot COOEt$ (*loc. cit.*), which boils at 157° under a pressure of 15 mm., has basic properties, and is unstable in the air; the *orthonitrobenzylidene* derivative is yellow, and melts at 85—86°. Ethylic phenylsemicarbazide-carboxylate, $NH_2\cdot CO\cdot NH\cdot NPh\cdot COOEt$ (*loc. cit.*), is better obtained by boiling phenylsemicarbazide (1 mol.) with ethylic chloroformate (2 mols.) in benzene solution; its melting point is now given as 172°; from it, 1-phenylurazole, $\begin{matrix} NPh\cdot CO \\ | \quad\quad\quad\;\; \\ NH{-}CO \end{matrix}\!\!>\!NH$, can be obtained by heating

with alkalis or alkali carbonates. On dissolving it in dilute hydrochloric acid and adding sodium nitrite, a reddish-yellow *nitroso*-derivative, melting and decomposing at about 75°, is obtained. In cooled ethereal solution, ethylic phenylhydrazidoformate (2 mols.) reacts with ethylic chloroformate (1 mol.), forming *phenylhydrazine-aβ-dicarboxylate*, $COOEt\cdot NH\cdot NPh\cdot COOEt$, which melts at 58—60°, yields diphenylcarbamide when heated with aniline, and the above mentioned biazolone when fused with acetamide; it can also be obtained by boiling ethylic phenylcarbazinate, $COOEt\cdot NH\cdot NHPh$, with ethylic chloroformate in benzene solution. The tetrazine described previously (*loc. cit.*) is identical with compounds to which slightly different formulæ have been assigned by Pinner (Abstr., 1888, 1084) and Heller (Abstr., 1891, 1213).   C. F. B.

Constitution of Phenylhydrazones. By PAUL C. FREER (*Amer. Chem. J.*, 1899, **21**, 14—64).—Phenylhydrazones are usually regarded as having the formula $CHRR' \cdot C(CR''_3){:}N \cdot NHPh$, but certain members of this class of substances appear to have a hydrazo-structure, $CRR' {:} C(CR''_3) \cdot NH \cdot NHPh$; the latter are readily oxidised to azo-compounds, whilst the true hydrazones do not undergo this change. The azo-compounds so obtained form perbromides; reduction with sodium amalgam reconverts both the azo-derivative and its perbromide into the original hydrazo-compound. The true hydrazones are either not affected by benzoic chloride or, if acted on by this reagent, they yield only benzoyl derivatives; the hydrazo-compounds, treated in a similar manner, give rise to dibenzoyl derivatives, and when these are unstable dibenzophenylhydrazide is the final product. The result of adding hydrocyanic acid to a hydrazone will be the same whichever of the above formulæ is assumed to be correct, hence this reaction cannot be used to distinguish between the two classes of compounds; moreover, the property of forming an additive compound is not a general one.

Dibenzophenylhydrazide is obtained by the action of benzoic chloride on the hydrazones of acetone and acetophenone, and benzoic anhydride behaves in a similar manner; neither of these hydrazones can be benzoylated by the Schotten-Baumann method. Benzaldehyde and phthalic anhydride decompose acetonephenylhydrazone, yielding benzylidenephenylhydrazone and phthalylphenylhydrazone respectively.

1 : 4-*Bromobenzeneazostyrene* (compare Abstr., 1897, i, 342), prepared from acetophenonephenylhydrazone, crystallises from petroleum in reddish prisms and melts at 48°, exploding violently when further heated; it is reconverted into the hydrazone by sodium amalgam. The perbromide resembles the corresponding acetone derivative, but is probably a mixture of two substances.

1 : 4-*Benzobromophenylhydrazide*, $C_6H_4Br \cdot NH \cdot NHBz$, which is formed by the action of bromine on an ethereal solution of benzophenylhydrazide, crystallises in lustrous, white leaflets melting at 156°.

1 : 4-*Benzoylazobromobenzene*, $C_6H_4Br \cdot N_2 \cdot COPh$, obtained by oxidising the preceding compound with mercuric oxide suspended in dry ether and concentrating the filtrate in a vacuum, forms red plates melting at 69°; when pure, it is stable; on heating, it gives off nitrogen at 133° and benzoic acid at 142°; on reduction with sodium amalgam, the hydrazide is regenerated. The *perbromide*, $C_{13}H_9N_2OBr,5Br$, formed on adding bromine to a chloroform solution of the azo-compound, crystallises in garnet-red prisms and melts and decomposes at 123°. Another *perbromide*, $C_{13}H_9N_2OBr,4Br$, is produced at the same time, and is also formed when the preceding compound is treated with cold alcohol; it is, moreover, the sole product when the reaction is performed in glacial acetic acid.

1 : 4-*Acetobromophenylhydrazide*, obtained in a similar manner to the benzoyl derivative, crystallises from alcohol in leaflets and melts at 161°. When treated with concentrated hydrocyanic acid, it yields a *hydrocyanide*, $C_{10}H_{12}BrN_3$, crystallising in hard prisms, and melting at 95—96°; when oxidised with mercuric oxide, the hydrazide is converted into a red oil which gives a yellow perbromide.

Pyruvic acid hydrazone does not behave like these hydrazo-compounds; it is not oxidised to an azo-compound on exposure to air, and on treatment with mercuric oxide it gives rise to a *substance* which is probably the acetophenylhydrazide of pyruvic acid hydrazone, $C_{17}H_{18}N_4O_2$, since it is hydrolysed by alkalis into acetophenylhydrazide and pyruvic acid phenylhydrazone. Benzylidenephenylhydrazone is also a true hydrazone, since it is not oxidised to an azo-compound. Some ketones and aldehydes appear to yield hydrazones belonging to both classes. Smith and Ransom (Abstr., 1894, i, 294) have already obtained two isomeric benzoinphenylhydrazones, and the author, by treating an ethereal solution of the β-compound with a small quantity of benzoic chloride, has now produced a third isomeride, *γ-benzoinphenylhydrazone*, which crystallises from alcohol in plates, and melts at 162°. Neither the α- nor the γ-compound reacts with benzoic chloride at ordinary temperatures. The β-isomeride, when oxidised by nitrous anhydride (?), yields a *substance* the composition of which corresponds with that required by the formula $C_{20}H_{16}N_6O_3$; it crystallises from alcohol in red needles decomposing at 137°. The α-isomeride, when similarly treated, does not yield a red substance, and the γ-compound is not affected by the oxides of nitrogen.

It appears probable that the β-modification has the hydrazo-structure, but the exact constitution of the three isomerides has yet to be determined.

Preliminary experiments on Fischer's two ethylidenephenylhydrazones (Abstr., 1896, i, 361) seem to indicate that the β-variety (m. p. 60°) is the hydrazo-compound, and that a third modification may exist which melts at 80°.

The compound, obtained by Hess from phenylhydrazine and bromacetophenone, when heated with glacial acetic acid or alcoholic hydrogen chloride, yields a *substance* having the composition $C_{20}H_{18}N_2$; this crystallises in white, silky needles and melts at 114°—115°.

The *compound*, NHPh·NH·CH₂·CH:N·NHPh, produced by the action of chloracetaldehyde hydrate and phenylhydrazine in alcoholic solution, forms colourless prisms and melts at 94°—95°; when boiled with alcohol or benzene, it seems to undergo polymerisation; sodium amalgam reduces it readily, forming symmetrical *diphenylethylenehydrazine*, $C_2H_4(NH·NHPh)_2$, which crystallises in white needles melting at 100°.   G. T. M.
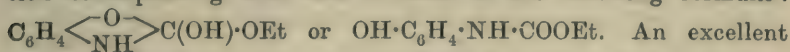

Salicylparaphenetidine and its Derivatives. By GIOVANNI BOLEZZI (*Gazzetta*, 1898, **28**, ii, 197—202).—Salicylparaphenetidine has been prepared by Scholvien by heating a mixture of paramidophenetoil and salicylic acid with phosphorus trichloride; by this method, a pure product cannot be obtained, owing to the separation of an oil. The author finds that by heating a mixture of salicylic acid and paraphenetidine sulphate, in molecular proportion, at 210°, the compound is obtained in a much cleaner form, and on crystallisation from dilute spirit, forms glistening laminæ, having a pearly lustre, and melting at 142—143° instead of 139·5°. It is soluble in alcohol, ether, and acetic acid, but insoluble in water, and yields

an *acetyl* derivative, $OEt \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_4 \cdot OAc$, which forms white, silky needles melting at 132°, and is soluble in alcohol or acetic acid. The *benzoyl* derivative, $OEt \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_4 \cdot OBz$, crystallises in silky needles, melts at 136—137°, and is insoluble in water, but soluble in alcohol, ether, and acetic acid. T. H. P.

Constitution of Salts of Imidoethers and other Carbimide Derivatives. By JULIUS STIEGLITZ (*Amer. Chem J.*, 1899, 21, 101—111).—This is a theoretical paper, bearing on the practical results described in the following abstract, and also on work not yet published; it deals with the constitution of the salts of carbimide bases. When carbimide derivatives combine with acids, the products are usually considered to contain quinquevalent nitrogen in the group $-\overset{v}{C} \vdots NRHCl$, but it is already admitted that sometimes the addition occurs at the double linking, as in the case of isocyanates, and the additive products of hydrocyanic acid and fulminic acid. It is assumed that the salts of the imidoethers, $OR \cdot RC \vdots NR$, the amidines $NHR \cdot RC \vdots NR$, the pyridines, and quinolines contain quinquevalent nitrogen doubly linked to carbon, $>C \vdots \overset{v}{N}RHCl$; the alternative constitution, $>\overset{III}{C}Cl \cdot NHR$, for these derivatives has not been considered. The hydrobromide of 1:2-chloromethenylamidophenol and the hydrochloride of the corresponding bromo-compound are identical, and they must have the formula $CClBr<^{NH}_{-O}>C_6H_4$. The hydroxides from the alkylquinolinium salts are now considered to contain the group $-\overset{III}{N}R \cdot CH(OH)-$ and not $-\overset{v}{N}R(OH) \vdots CH-$, and it seems quite likely that their salts may also have a constitution corresponding with the former of these formulæ. G. T. M.

Hydrochlorides of Carbophenylimido-derivatives. By HERBERT N. McCoy (*Amer. Chem. J.*, 1899, 21, 111—167. Compare preceding abstract).—3 : 5-*Dibromocarboxylamidophenol*, produced by the action of potassium hypobromite on salicylamide, crystallises in needles and melts at 250°; it is not identical with the dibromocarbonylamidophenol (m. p. 243—245°) obtained by Jakoby by the direct bromination of carbonylamidophenol. Both isomerides are readily reduced to the latter substance by sodium amalgam. The 3:5-compound may be synthesised from 3 : 5-dibromosalicylamide. The *alkali* salts of both isomerides are described. 1 : 2-Carbonylamidophenol is best prepared by Bender's method from so-called ethylic 1 : 2-amidophenylic carbonate; the latter substance is insoluble in acids but dissolves readily in alkalis, and is really a hydroxy-compound obtained by intramolecular rearrangement from the initially formed amidocarbonate, $NH_2 \cdot C_6N_4 \cdot O \cdot COOEt$, and having a constitution corresponding with one or other of the following formulæ : $C_6H_4<^{-O-}_{NH}>C(OH) \cdot OEt$ or 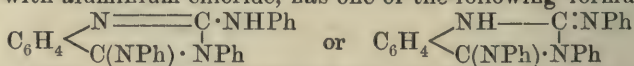$OH \cdot C_6H_4 \cdot NH \cdot COOEt$. An excellent yield of 1 :2-chloromethenylamidophenol is obtained by passing dry chlorine into a cold solution of 1 : 2-thiocarbamidophenol in chloro-

form, and the 1 : 2-*bromomethenylamidophenol*, $C_6H_4\underset{O}{\overset{N}{<}}>CBr$, obtained by the substitution of bromine for chlorine in this reaction, forms white crystals melting at 27°. These substances are not produced by the action of the phosphorus halogen compounds on 1 : 2-carbonylamidophenol. 1 : 2-*Chloromethenylamidophenol hydrochloride* (1 : 2-dichlorocarbonylaminophenol), $C_6H_4\underset{-O-}{\overset{NH}{<}}>CCl_2$, prepared by passing hydrogen chloride into a solution of the chloromethenyl compound in petroleum, forms white crystals melting at 57—58° ; it is very unstable, and can only be kept in an atmosphere of hydrogen chloride. The *nitrate* forms white crystals and the *platinochloride* is orange coloured ; both salts are decomposed by water. The *hydrobromide* (1 : 2-*chlorobromocarbonylamidophenol*), $C_6H_4\underset{O}{\overset{NH}{<}}>CClBr$, is more stable than the hydrochloride, and decomposes at 155° ; it is prepared either by adding hydrogen bromide to chloromethenylamidophenol, or hydrogen chloride to the bromo-derivative ; water decomposes it into the chloro-derivative and hydrogen bromide. 1 : 2-*Bromomethenylamidophenol hydrobromide* (1 : 2-dibromocarbonylamidophenol) melts at 163°, and is also decomposed by water.

The compound, $C_{26}H_{20}N_4$, obtained by condensing carbodiphenylimide with aluminium chloride, has one of the following formulæ :

$$C_6H_4\underset{C(NPh)\cdot NPh}{\overset{N=\!=\!=\!=C\cdot NHPh}{<}} \quad \text{or} \quad C_6H_4\underset{C(NPh)\cdot NPh}{\overset{NH\!-\!-\!-C:NPh}{<}}$$

(Abstr., 1897, i, 422, 490). The latter is now shown to be more probable. The compound, on hydrolysis, yields a substance, $C_{20}H_{15}N_3O$, which is either $C_6H_4\underset{CO-NPh}{\overset{N=C\cdot NHPh}{<}}$ or $C_6H_4\underset{CO\cdot NPh}{\overset{NH\cdot C:NPh}{<}}$. This when heated with methylic iodide for 9 hours at 100°, yields a *methyl* derivative which crystallises in colourless needles melting at 174°. The latter compound, on hydrolysis, yields aniline and 1′-methyl-2′ : 4-diketo-3′-phenyltetrahydroquinazoline, which melts at 223°, and is identical with the product obtained by methylating 2′ : 4-diketo-3′-phenyltetrahydroquinazoline. Fortmann gives 233° as the melting point for this compound.

2′-*Methylanilido*-3′-*phenyl*-4-*ketodihydroquinazoline*,

$$C_6H_4\underset{CO\cdot NPh}{\overset{N=C\cdot NMePh}{<}},$$
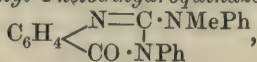
the isomeride of the above methyl derivative, obtained by heating 2′-chloro-3′-phenyl-4-ketodihydroquinazoline with methylaniline at 180° for 2 hours, crystallises from dilute methylic alcohol or from ether and petroleum in needles melting at 123°.

The two modifications of 2′ : 4′-diphenylimido-3′-phenyltetrahydroquinazoline behave differently towards phenylcarbimide ; the α-form yields a phenylcarbamide derivative, whereas the β-form does not.

2′-*Methylthio*-3′-*phenyl*-4′-*ketodihydroquinazoline*, $C_6H_4\underset{N\;:\;C\cdot SMe'}{\overset{CO\cdot NPh}{<}}$ obtained on treating 2′-thio-3′-phenyl-4′-ketotetrahydroquinazoline with

methylic iodide and alcoholic potash, forms long needles melting at 125°. Its isomeride, the nitrogen ether, melts at 288—289°.

2′-*Methoxy*-3′-*phenyl*-4′-*ketodihydroquinazoline*, $C_6H_4 \begin{smallmatrix} N=C \cdot OMe \\ \\ CO \cdot NPh \end{smallmatrix}$,

from 2′-chloro-3′-phenyl-4′-ketodihydroquinazoline and sodium methoxide, crystallises in rhombohedra and melts at 134°. G. T. M.

Mercurio-methacetin [-paracetamidophenylic methylic ether] and Mercurio-α-acenaphthalide. By L. PRUSSIA (*Gazzetta*, 1898, **28**, ii, 122—129).—*Mercurio-methacetin*, $Hg(NAc \cdot C_6H_4 \cdot OMe)_2$, separates in tufts of slender, colourless needles melting at 191·5°, on filtering and cooling a hot solution of methacetin and mercuric chloride to which sodium carbonate has been added. It is decomposed by cold chloroform or by hot ethylic or methylic alcohol, benzene, or water; its composition was proved by treating it with sodium thiosulphate, potassium iodide, and ammonium bromide; in each case, methacetin and alkali are liberated.

Mercurio-α-acenaphthalide, $Hg(NAc \cdot C_{10}H_7)_2$, prepared by a method analogous to that described above, crystallises in microscopic laminæ, apparently rhombic, which soften at 199° and melt at 202°. It is soluble in boiling water, but alcohol decomposes it; it is insoluble in ether. T. H. P.

Organo-mercuric Compounds of Diphenylamine. By L. PRUSSIA (*Gazzetta*, 1898, **28**, ii, 129—132. Compare Abstr., 1897, i, 337).—Diphenylamine reacts with mercuric salts giving compounds containing mercury, one atom combined directly with basic nitrogen and another with the aromatic nuclei. All these compounds contain a bivalent radicle of the constitution $Hg \begin{smallmatrix} C_6H_4 \cdot NHPh \\ \\ C_6H_4 \cdot NHPh \end{smallmatrix} Hg$, which the author terms paramercuriodiphenylenediphenylmercuriodiammonium. The *hydroxide* of this base, $Hg(C_6H_4 \cdot NHPh \cdot OH)_2Hg$, formed by treating the corresponding acetate with strong caustic potash solution, is a white, granular, amorphous substance which is almost insoluble in all the ordinary solvents, and its aqueous and alcoholic solutions have an alkaline reaction. It decomposes at above 200° without melting. The *acetate*, $Hg(C_6H_4 \cdot NHPh \cdot OAc)_2Hg$, which separates on mixing alcoholic solutions of mercuric acetate and diphenylamine, crystallises from boiling alcohol in glistening, colourless laminæ melting at 178°; it is insoluble in water, but fairly soluble in boiling ethylic alcohol, or in benzene. The *chloride*, $Hg(C_6H_4 \cdot NHPhCl)_2Hg$, prepared by mixing alcoholic solutions of the acetate and calcium chloride, forms a microscopic, colourless, nodular mass which softens at 232° and decomposes at above 240° without melting; it is sparingly soluble in methylic and ethylic alcohol, chloroform, benzene, and ether, and is insoluble in water. Sodium thiosulphate converts the hydroxide into *paramercuriodiphenylamine*, $Hg(C_6H_4 \cdot NHPh)_2$, which separates from boiling benzene in rose-coloured tufts and melts at 182·5°.
T. H. P.

Organo-mercuric Compounds of Diphenylmethylamine. By G. GARBARINI (*Gazzetta*, 1898, **28**, ii, 132—134. Compare previous abstract).—Diphenylmethylamine, with mercury salts, yields com-

pounds analogous to those formed by diphenylamine. These compounds contain the bivalent radicle, $Hg{<}^{C_6H_4\cdot NMePh}_{C_6H_4\cdot NMePh}{>}Hg$, which the author terms paramercuriodiphenylenediphenyldimethylmercuriodiammonium.

The *hydroxide* of this base, $Hg(C_6H_4\cdot NMePh\cdot OH)_2Hg$, formed by acting on the corresponding acetate with caustic potash, is a white, amorphous mass, insoluble in the ordinary solvents. The *acetate*, $Hg(C_6H_4\cdot NMePh\cdot OAc)_2Hg$, prepared by mixing alcoholic solutions of diphenylmethylamine and mercuric acetate, crystallises from boiling alcohol in colourless needles melting at 128°. It is insoluble in water and benzene, and only slightly soluble in methylic or ethylic alcohol. On treating an aqueous solution of the hydroxide with sodium thiosulphate solution, paramercuriodiphenylmethylamine is deposited, and crystallises from a mixture of benzene and light petroleum in colourless laminæ melting at 138—139°. T. H. P.

Antimonylphenolic Compounds. By Henri Causse (*Ann. Chim. Phys.*, 1898, [vii], **14**, 526—564. Compare Abstr., 1892, 1078; 1898, i, 470).—*Antimonylcatechol acetate*, $.C_6H_4{<}^O_O{>}Sb\cdot OAc$, is obtained by the action of acetic anhydride on a solution of the hydroxide in glacial acetic acid in the presence of a trace of acetic chloride. The group $Sb\cdot OH$ appears to be linked to both oxygen atoms of the catechol molecule, for when acetaldehyde is added to a solution of this phenol containing a halogen salt of antimony, no acetal compound is produced. Antimonylpyrogallol hydroxide is obtained by the action of pyrogallol on a solution of antimony oxide in tartaric acid (Abstr., 1893, i, 75). The *chloride*, $OH\cdot C_6H_4{<}^O_O{>}SbCl$, is best obtained by the action of antimony chloride on pyrogallol in methylic alcohol solution; the *bromide* is produced in a similar manner; it crystallises from dilute hydrobromic acid; the *iodide* is readily decomposed by water into a mixture of hydroxide and basic iodide; the *fluoride* is easily obtained by mixing solutions of antimony fluoride and pyrogallol, and crystallises from dilute hydrofluoric acid. These four salts form colourless crystals, closely resembling each other in physical and chemical properties. The *oxalate* is produced by adding a strong solution of potassium hydrogen oxalate to a solution of the chloride in dilute hydrochloric acid.

The *hydroxide*, $COOMe\cdot C_6H_2(OH){<}^O_O{>}Sb\cdot OH$, produced by mixing alcoholic solutions of methylic gallate and antimony chloride, separates as a white, crystalline powder which is freed from antimony chloride by washing with alcohol, and from antimonylphenolic chloride by treatment with hot water. Hydrochloric acid converts it into the *chloride*. The corresponding hydroxide from gallic acid has long been known; the *chloride*, $COOH\cdot C_6H_4(OH){<}^O_O{>}SbCl$, the *bromide*, and the *potassium* salt, $COOK\cdot C_6H_4(OH){<}^O_O{>}Sb\cdot OH$, are now described for the first time. Catechol may be separated from

its isomerides by the addition of antimony fluoride to an aqueous solution of the three compounds when antimonylcatechol fluoride is precipitated ; the filtrate is treated with acetaldehyde, which removes resorcinol in the form of its acetal ; the quinol in the final mother liquor is oxidised to insoluble quinhydrone by the addition of iodic acid. G. T. M.

Synthesis of Hydroxyaldehydes of the Benzene Series. By LUDWIG GATTERMANN and M. KÖBNER (*Ber.*, 1899, **32**, 278—283).— The authors find that the presence of aluminium chloride is not necessary, as was formerly thought (Gattermann and Berchelmann, Abstr., 1898, i, 561), for the preparation of hydroxy-aldehydes by the interaction of phenols with hydrogen cyanide, in presence of hydrogen chloride ; zinc chloride, in most cases, produces the same result, whilst in a few instances, notably with resorcinol, orcinol, and phloroglucinol, no condensing agent at all is necessary. When either of the new modifications is adopted, ether can be employed as the solvent instead of benzene, as was formerly necessary ; the method is thus rendered more suitable for the treatment of polyatomic phenols, which are sparingly soluble in benzene. The yield in most cases is nearly quantitative.

The crystalline *imide-hydrochloride*, $C_6H_3(OH)_2 \cdot CH:NH,HCl$, which separates initially (compare Gattermann, Abstr., 1898, i, 476) in the preparation of 1 : 3 : 4-dihydroxybenzaldehyde from resorcinol by the above method, dissolves unchanged in cold water, but is decomposed by warm, giving rise to ammonium chloride and the corresponding aldehyde.

The *imide-hydrochloride* derived from phloroglucinol is, however, not decomposed by hot water, and is converted by dilute sulphuric acid into the corresponding *sulphate*, $[C_6H_2(OH)_3 \cdot CH:NH]_2,H_2SO_4$, which dissolves only sparingly in water ; when the hydrochloride is boiled with dilute sulphuric acid, it is converted into 1 : 3 : 5 : 2-*trihydroxybenzaldehyde*. This crystallises from water in colourless needles containing $2H_2O$, softens when heated at 105°, and melts at no definite temperature ; the aqueous solution of the aldehyde has a bitter taste, and produces, with ferric chloride, a wine-red coloration which remains unchanged on adding caustic soda.

The *imide-hydrochloride*, $C_7H_8NClO_3$, obtained from pyrogallol, is easily soluble in cold water, but separates from the aqueous solution, on adding ether, in colourless crystals which melt indefinitely at about 120°. The *phenylhydrazone*, $C_{13}H_{12}N_2O_3$, of 1 : 2 : 3 : 4-trihydroxybenzaldehyde (Abstr., 1898, i, 581) forms yellow leaflets which melt at 161°.

2 : 4 : 5-*Trihydroxybenzaldehyde*, prepared from hydroxyquinol (Thiele, Abstr., 1898, i, 469) crystallises from water in thick, pointed prisms, and melts at 223° ; with ferric chloride, it produces an intensely green coloration, which, in presence of caustic soda, becomes reddish brown, whilst with lead acetate and with baryta water it gives rise to yellow precipitates ; the *phenylhydrazone*, $C_{13}H_{12}N_2O_3$, forms yellowish leaflets and melts at 200°. W. A. D.

Synthesis of Daphnetin and Æsculetin. By LUDWIG GATTER-MANN and M. KÖBNER (*Ber.*, 1899, **32**, 287—288).—2 : 3 : 4-Tri-hydroxybenzaldehyde (Abstr., 1898, i, 581), when heated with sodium acetate and acetic anhydride during 5 hours at 170—180°, gives rise to diacetodaphnetin, which, on hydrolysis, yields daphnetin identical with the natural product : von Pechmann's views as to the structure of the latter (Abstr., 1884, 1173) are thus confirmed. By a similar reaction, 2:4:5-trihydroxybenzaldehyde (preceding abstract) is converted into the diacetyl derivative of æsculetin, which is thus shown to have the structure, $C_6H_2(OH)_2 <^{O-CO}_{CH:CH}$ [$(OH)_2 : O : CH = 1:2:4:5$], attributed to it by Will. W. A. D.

Electrolytic Decomposition of Orthonitrobenzoic Acid. By CARL SCHALL (*Chem. Centr.*, 1898, ii, 1043 ; from *Arch. Sci. phys. nat. Genève* [iv], **6**, 387—388).—When solutions of the salts of certain aromatic acids in the acids themselves are electrolysed, hydrocarbons are formed ; such solutions are prepared by dissolving sodium car-bonate in the dry molten acid. When a solution of 6·4 grams of sodium carbonate in 50 grams of orthonitrobenzoic acid at 160—180° is electrolysed by a current of 0·4—1 ampère, brown flakes, black car-bonaceous substances, and small quantities of crystals which melt at 149—150° and have no acid properties are obtained. When water is present, nitrophenols are also formed. E. W. W.

New Derivatives of Gallic Acid. By A. MAX HAMBURG (*Monatsh.*, 1898, **19**, 593—608).—*Methylic bromotrimethylgallate,* $C_6HBr(OMe)_3 \cdot COOMe$, is prepared by adding bromine to methylic tri-methylgallate dissolved in cooled, dry carbon tetrachloride ; dry air is then driven through the liquid and the product distilled under diminished pressure. It is a colourless, highly dispersive, oily liquid, which boils at 202° under a pressure of 16 mm., and dissolves readily in the ordinary solvents, excepting water. When heated with potassium methoxide at 160° in sealed tubes, it is to a great extent decomposed, and a substance, probably *bromotrimethylgallic acid,* $C_6HBr(OMe)_3 \cdot COOH$, is formed in small quantity. This separates from alcohol, on the addition of water, as white, silky, shining needles, melts at 151°, and dissolves readily in alcohol and ether, less readily in benzene, and is insoluble in water.

Methylic nitrotrimethylgallate, $NO_2 \cdot C_6H(OMe)_3 \cdot COOH$, is prepared from methylic trimethylgallate, dissolved in acetic anhydride, by the action of nitric acid saturated with nitrous acid. It crystallises in yellowish tablets, melts at 67°, and dissolves readily in alcohol and ether, but is nearly insoluble in water, and in dilute potash.

When methylic nitrotrimethylgallate is heated with an alcoholic solution of stannous chloride, it is quickly reduced, and the *stanno-chloride* of the product separates in a crystalline form. The *hydro-chloride* of methylic amidotrimethylgallate separates from methylic alcohol in pyramidal crystals belonging to the rhombic system [$a:b:c=1:0·6486:0·9490$]; it is insoluble in ether, but dissolves

readily in water or alcohol, and the solution in the latter has a blue fluorescence; it melts at 167°. *Methylic amidotrimethylgallate*, $NH_2 \cdot C_6H(OMe)_3 \cdot COOMe$, crystallises from a mixture of benzene and light petroleum in well-formed, faintly-coloured crystals belonging to the monoclinic system $[a : b : c = 0.3998 : 1 : 0.2917, \ ac = 97° 14']$. It is readily soluble in alcohol, ether, and benzene, and dissolves in warm petroleum, but is only very sparingly soluble in water; it melts at 41°.

Methylic hydroxytrimethylgallate, $OH \cdot C_6H(OMe)_3 \cdot COOMe$, obtained by warming the solution of the corresponding diazo-compound, separates from a mixture of methylic alcohol and light petroleum in colourless crystals melting at 85°. It is nearly insoluble in water, but dissolves readily in alcohol, ether, and benzene, and sparingly in methylic alcohol and light petroleum. *Hydroxytrimethylgallic acid*, $OH \cdot C_6H(OMe)_3 \cdot COOH$, is purified by conversion into the corresponding calcium salt, from which it may be recovered by the addition of hydrochloric acid. It crystallises from boiling petroleum in slender, silky, white needles, which gradually become coloured on exposure to the air; it melts and decomposes at 191°, is sparingly soluble in water or light petroleum, but dissolves readily in warm alcohol, ether, benzene, or alkalis. Both the acid and its methylic salt yield gallic acid when heated with hydriodic acid at 127—135°.

A. L.

Preparation of Homophthalic Acid [Orthocarboxyphenyl-acetic Acid] and β-Hydrindone from the Indene of Coal Tar. By FRIEDRICH HEUSLER and HEINRICH SCHIEFFER (*Ber.*, 1899, **32**, 28—34).—Some of the fraction of coal-tar oil which is rich in indene is made into an emulsion with water by means of a mechanical stirrer, and a slight excess of 6 per cent. potassium permanganate is added gradually, no heat being employed. The product is filtered, and the filtrate shaken with benzene; the orthocarboxyphenyl-acetic (homophthalic) acid is then obtained by prolonged extraction with ether. The method is probably an advantageous one for the preparation of the acid. If cooling with ice is employed during the oxidation, a certain amount of hydrindeneglycol is formed; it can be separated by extraction with chloroform.

When chlorhydroxyhydrindene, obtained by chlorinating this fraction of coal-tar oil and then boiling it with water, is boiled with methyl alcoholic sodium methoxide, it forms the *hydrindeneglycol monomethylic ether*, $C_6H_4{<}^{CH(OMe)}_{CH_2-}{>}CH \cdot OH$; this boils at 150—151° under a pressure of 13·5 mm., and has a sp. gr. = 1·12 at 20°; when boiled for a short time with 25 per cent. sulphuric acid, it yields *β-hydrindone*, $C_6H_4{<}^{CH}_{CH_2}{>}CO$. If this is left in contact for 2 days with very dilute caustic soda, it forms *anhydrobis-β-hydrindone*, $C_9H_{14}O$, melting at 170°, and when treated, in alcoholic solution, with amylic nitrite and a little hydrochloric acid, it yields *di-isonitroso-β-hydrindone*, melting and decomposing at 233°. When the hydrindone is dissolved in fuming nitric acid and the solution poured into water, yellow 4-*nitro-*

β-hydrindone, $NO_2 \cdot C_6H_3 \overset{CH_2}{\underset{CH_2}{\diagdown}} CO$, melting at 141—141·5° is formed;
this dissolves in caustic soda, forming a deep purple-red solution; when left with dilute nitric acid for a day, 1 : 2 : 4-nitrophthalic acid is obtained, but if it is oxidised with chromic acid in acetic acid solution 1 : 2 : 4-nitro-orthocarboxyphenylacetic acid, $COOH \cdot C_6H_3(NO_2) \cdot CH_2 \cdot COOH$, is formed as an intermediate product.   C. F. B.

Isomeric Forms of Ethylic Benzylidenebisacetoacetate.   By ROBERT SCHIFF (*Ber.*, 1899, **32**, 332—337).—Besides the ordinary form of diethylic benzylidenebisacetoacetate, $CHPh(CHAc \cdot COOEt)_2$, which melts at 151° (Hantzsch, Abstr., 1886, 77), a second form has recently been prepared by Rabe (this vol., i, 289) from the sodium salt, an observation which is confirmed by the author in the present paper.   He shows further that the three substances melting at 150°, 134°, and 120°, which he obtained by the action of sodium ethoxide on the three modifications of ethylic benzylideneanilinoacetoacetate melting at 104°, 78°, and 95° (Abstr., 1898, i, 355), are different forms of ethylic benzylidenebisacetoacetate, and not of ethylic phenylcarbinolacetoacetate, as was previously supposed.   In the preparation of ethylic benzylidenebisacetoacetate by the condensation of benzaldehyde with ethylic acetoacetate in presence of a trace of piperidene or of dipropylamine, the author states that the three modifications melting at 150°, 134°, and 120° are all produced, together with an isomeric mixture melting at 90—112°.   All the different modifications, on boiling with acetic anhydride, are converted into the form melting at 151°.   The constitution of the different modifications has not been ascertained.   T. M. L.

Action of Ethylic Acetoacetate on Benzidine.   By KARL HEIDRICH (*Monatsh.*, 1898, **19**, 690—706).—Ethylic acetoacetate unites with benzidine at 100°, forming the compound, $2C_{12}H_8(NH_2)_2, C_6H_{10}O_3$, which crystallises in small, yellow plates melting at 128°.   At 120°, however, *diacetoacetic benzidide*, $C_{12}H_8(NH \cdot CO \cdot CH_2Ac)_2$, is formed by elimination of water; this crystallises in thin, lustrous needles, melts and decomposes at 233—235°, and is sparingly soluble in the usual solvents.   It gives a violet coloration with alcoholic ferric chloride, and reduces ammoniacal silver oxide.   Bromine converts it into a *dibromo*-derivative, $C_{20}H_{18}Br_2N_2O_4$, which crystallises in small, lustrous needles, and decomposes at about 250°.   It contains two atoms of replaceable hydrogen, and yields a *sodium* derivative, which crystallises in small needles, is decomposed by water, and with ethylic iodide yields the *diethyl* derivative, which melts and decomposes above 300°. The *monophenylhydrazone*, $C_{26}H_{26}N_4O_3$, forms white, granular crystals, and decomposes at 250°.   When treated with concentrated sulphuric acid in the cold, diacetoacetic benzidide is converted into *dihydroxy-dilepidine*, $C_{20}H_{16}N_2O_2$, which is an amorphous, white powder, melts above 300°, and gives no coloration with ferric chloride.

Monacetoacetic benzidide, $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_2Ac$, is always formed in small amount in the interaction of ethylic acetoacetate with benzidine; it is soluble in acids and can thus be separated from the insoluble diacetoacetic benzidide.   It forms small, granular crystals,

decomposes at 300°, and gives a violet coloration with ferric chloride. The *hydrochloride*, *sulphate*, and *nitrate* are crystalline, and dissolve sparingly in water. When treated with sulphuric acid, it yields 3-*amido-phenyl-2'-hydroxylepidine*, $C_{16}H_{14}N_2O$, which forms white granules and gives a violet coloration with ferric chloride. A. H.

Orthophenylbenzaldehyde. By RICHARD FANTO (*Monatsh.*, 1898, **19**, 584—592).—*Orthophenylbenzaldehyde*, $C_{13}H_{10}O$, is made by heating an intimate mixture of calcium orthophenylbenzoate with calcium formate, a considerable quantity of diphenyl being formed simultaneously. It is a pale, yellowish-green, odourless liquid, denser than water, and dissolves in all proportions in alcohol, ether, chloroform, and benzene, but only very sparingly in water; it boils at 184° under 21 mm. pressure. When oxidised with chromic acid, it yields ortho-phenylbenzoic acid. The *oxime*, $C_{12}H_9 \cdot CH\!:\!NOH$, has a faint, fruity odour, crystallises from ether in slender, white needles, and melts at 115°; it dissolves readily in alcohol, ether, chloroform, and benzene, but is insoluble in water. The *phenylhydrazone*, $C_{12}H_9 \cdot CH\!:\!N \cdot NHPh$, which is very unstable, crystallises from cooled ether in shining leaflets and melts at 118—124°.

When an alcoholic solution of orthophenylbenzaldehyde is treated with sodium amalgam, care being taken that the liquid remains neutral, and this is subsequently extracted with ether, a crystalline *substance*, $C_{26}H_{18}O$, and an oil are obtained; the crystalline substance separates from alcohol in small, glistening crystals, has a pleasant, rose-like odour, and melts at 111°, decomposing at higher temperatures; it dissolves very readily in ether and light petroleum, but only sparingly in alcohol. The oil, when treated with acetic anhydride and submitted to distillation, yields *orthophenylbenzylic acetate*, $C_{12}H_9 \cdot CH_2 \cdot OAc$, a thick, odourless, pale yellow oil which boils at 182° under 20 mm. pressure; it is miscible with ether, alcohol, and petroleum, but insoluble in water. *Orthophenylbenzylic alcohol*, $C_{12}H_9 \cdot CH_2 \cdot OH$, prepared by hydrolysing the acetate with water at 130°, is a colourless, oily liquid, having an aromatic odour, and boils at 181° under 8 mm. pressure; it dissolves in all proportions in alcohol, ether, and benzene, but is insoluble in water. A. L.

Two Isomeric Chlorodiphenacyls. By CARL PAAL and HERMANN STERN (*Ber.*, 1899, **32**, 530—531. Compare Paal and Demeler, Abstr., 1896, i, 687).—Chlorodiphenacyl, $C_{16}H_{13}ClO_2$, melting at 117°, is prepared, according to Staedel and Rügheimer's directions, by the action of ammonia on an ethereal solution of chloracetophenone; it can also be obtained by the action of alcoholic sodium ethoxide on chloracetophenone. The isomeride melts at 154—155°, and both compounds yield diphenacyl on reducing the alcoholic solutions with zinc dust. M. O. F.

Iododiphenacyl. By CARL PAAL and HERMANN STERN (*Ber.*, 1899, **32**, 532—533).—*Phenacylic iodide* (ω-*iodacetophenone*), $COPh \cdot CH_2I$, is prepared by the action of aqueous potassium iodide on an alcoholic solution of chloracetophenone or bromacetophenone; it dissolves very readily in organic solvents, and has not been obtained pure.

Iododiphenacyl, $C_{16}H_{13}IO_2$, obtained by treating the foregoing substance with alcoholic sodium ethoxide, crystallises from alcohol in slender needles and melts at 215°.   . M. O. F.

Derivatives of Benzophenone. By PIETRO BARTOLOTTI (*Gazzetta*, 1898, 28, ii, 283—290).—*Benzoylcreosol benzoate,* $C_6H_2BzMe(OMe)\cdot OBz$ [Me : OMe : OBz = 1 : 3 : 4], prepared by the action of creosol benzoate on benzoic chloride in presence of zinc chloride, forms white crystals melting at 95—96°.

Benzoylcreosol, $C_6H_2BzMe(OMe)\cdot OH$, obtained by hydrolysing a hot alcoholic solution of benzoylcreosol benzoate with hot dilute alcoholic caustic soda, forms white crystals melting at 150°; it is soluble in the ordinary solvents but insoluble in water. It dissolves in sodium hydroxide solution, giving an intensely yellow liquid from which it is thrown down in the crystalline state by carbonic anhydride. Ferric chloride added to its dilute alcoholic solution produces a greenish coloration.

Benzoylcreosol acetate, $C_6H_2BzMe(OMe)\cdot OAc$, produced by the action of acetic anhydride on benzoylcreosol in presence of fused sodium acetate, separates from alcohol in white crystals melting at 77·5°.

Benzoylmethylcreosol, $C_6H_2BzMe(OMe)_2$, obtained by the action of methyl alcoholic potash and methylic iodide on benzoylcreosol, was not obtained crystalline.   T. H. P.

New Syntheses in the Flavone Group. By STANISLAUS VON KOSTANECKI (*Chem. Centr.*, 1898, ii, 1060 ; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 403—404).—Orthohydroxybenzylideneacetophenone dibromide, when treated with alcoholic potash, yields flavone, and, similarly, 2-bromoflavone is obtained from 5-bromo-2-hydroxybenzylideneacetophenone dibromide. Attempts to prepare 3 : 4-dihydroxyflavone from piperonal-2-hydroxyacetophenone dibromide resulted in the formation of piperonalcoumaranone, and 2-hydroxyanisalacetophenone dibromide and piperonalresacetophenone methylic ether yielded similar compounds and not flavone derivatives (compare the following abstracts).   E. W. W.

Ethoxy- and Methoxy-piperonalcoumaranone. By T. EMILEWICZ and STANISLAUS VON KOSTANECKI (*Ber.*, 1899, 32, 309—314. Compare Abstr., 1898, i, 369).—The compound, $C_{18}H_{14}O_5$, described by the authors as a product of the action of alcoholic potash on the acetyl derivative of piperonalresacetophenone ethylic ether, is shown to be 3-

ethoxypiperonalcoumaranone, $OEt\cdot C_6H_3\!\!<\!\!^{O}_{CO}\!\!>\!\!C\!:\!CH\cdot C_6H_3\!\!<\!\!^{O}_{O}\!\!>\!\!CH_2$;

thus the piperonal compound differs from the corresponding benzylidene compound by condensing to a 5-, and not to a 6-membered, ring. The substance crystallises from alcohol in long, straw-coloured needles, melts at 150°, and dissolves in concentrated sulphuric acid with an eosin-red colour.

Benzylidenepaeonol [*4-methoxy-2-hydroxyphenyl styryl ketone*],
$$OMe\cdot C_6H_3(OH)\cdot CO\cdot CH\!:\!CHPh,$$
separates from alcohol in long, deep-yellow needles which melt at 105°, and are coloured red by concentrated sulphuric acid. The *acetyl*

derivative crystallises from alcohol in pale yellow needles melting at 83—84°, and yields a colourless *dibromide* melting at 130·5—131·5°. The dibromide is converted, by the action of alcoholic potash, into 3-*methoxy-flavone*, $OMe \cdot C_6H_3 \underset{CO \cdot CH}{\overset{O—CPh}{<}}$; this crystallises from alcohol in colour-less needles melting at 110—111°, and like 3-ethoxyflavone, shows a very characteristic blue fluorescence when dissolved in concentrated sulphuric acid.

Piperonalpaeonol [4-*methoxy*-2-*hydroxyphenyl piperonalmethyl ketone*], $OMe \cdot C_6H_3(OH) \cdot CO \cdot CH:CH \cdot C_6H_3 \overset{O}{\underset{O}{<}} CH_2$, crystallises from alcohol in long, yellow needles which melt at 148·5°, and are coloured red by concentrated sulphuric acid. The *acetyl* derivative crystallises from alcohol in yellow needles melting at 158—159°, and yields a *dibromide* which crystallises from a mixture of chloroform and ether in colourless needles melting at 137—138°. By the action of alcoholic potash, the dibromide is converted into 3-*methoxypiperonalcoumaranone*; this has already been prepared by Friedländer and Brüll (Abstr., 1897, i, 221), but was described by them as a flavone derivative; it crystallises from alcohol in yellow needles, melts at 176°, and dissolves in concentrated sulphuric acid with an eosin-red colour.

The flavones are readily decomposed by sodium ethoxide in alcoholic solution, yielding a hydroxy-ketone and an aromatic acid; the isomeric coumaranone derivatives are converted into insoluble resins.

T. M. L.

Piperonalcoumaranone. By W. FEUERSTEIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1899, **32**, 315—317. Compare preceding abstract). —*Piperonal*-2′-*hydroxyacetophenone* [*orthohydroxyphenyl piperonalmethyl ketone*], $HO \cdot C_6H_4 \cdot CO \cdot CH:CH \cdot C_6H_3 \overset{O}{\underset{O}{<}} CH_2$, crystallises from alcohol in deep-yellow needles which melt at 137—138°, and are coloured red by concentrated sulphuric acid. The *acetyl* derivative crystallises from dilute alcohol in pale yellow needles melting at 95—96·5°, and yields a *dibromide* which crystallises from ether in colourless prisms melting at 113—114°. By the action of alcoholic potash, the dibromide is converted into *piperonalcoumaranone*, $C_6H_4 \underset{CO}{\overset{O}{<}} C:CH \cdot C_6H_3 \overset{O}{\underset{O}{<}} CH_2$; this crystallises from glacial acetic acid in deep-yellow needles melting at 192°; the crystals are coloured deep-red by concentrated sulphuric acid and yield an eosin-red solution; the substance is identical with that previously described by Friedländer and Neudörfer (Abstr., 1897, i, 425) as methylenedihydroxyflavone. T. M. L.

4-Methoxybenzylidenecoumaranone. By F. HERSTEIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1899, **32**, 318—321. Compare preceding abstracts).—*Anisylidene*-2-*hydroxyacetophenone* [*orthohydroxy-phenyl paramethoxystyryl ketone*], $OH \cdot C_6H_4 \cdot CO \cdot CH:CH \cdot C_6H_4 \cdot OMe$, crystallises from alcohol in bright, orange-coloured plates, melts at 93—94°, and is coloured red by concentrated sulphuric acid. The *acetyl* derivative crystallises in colourless prisms melting at 84°, and

yields a *dibromide* which crystallises from a mixture of chloroform and ether in white, silky needles melting at 104—105°. By the action of alcoholic potash, the dibromide is converted into *para-anisylidenecoumaranone*, $C_6H_4\!<^{O}_{CO}\!>C\!:\!CH\cdot C_6H_4\cdot OMe$, which crystallises from alcohol in long, yellow needles melting at 133·5—134·5°; the crystals are coloured red by concentrated sulphuric acid, and yield an orange-coloured solution.

4-*Ethoxybenzylidene*-2-*hydroxyacetophenone* [*orthohydroxyphenyl par-ethoxystyryl ketone*] crystallises from alcohol in yellow needles, melts at 61°, and is coloured red by concentrated sulphuric acid. The *acetyl* derivative crystallises from dilute alcohol in pale yellow flakes, and melts at 68°, but the dibromide has not yet been obtained in a crystalline form. T. M. L.

3:4′-Dihydroxyflavone. By STANISLAUS VON KOSTANECKI and F. W. OSIUS (*Ber.*, 1899, **32**, 321—325. Compare Abstr., 1898, i, 369 and 583).—*Anisylidenepaeonol* [4-*methoxy*-2-*hydroxyphenyl para-methoxystyryl ketone*], $OMe\cdot C_6H_3(OH)\cdot CO\cdot CH\!:\!CH\cdot C_6H_4\cdot OMe$, crystallises in yellow needles, and melts at 113—114°; the crystals are coloured red by concentrated sulphuric acid, and give an orange-coloured solution. The *acetyl* derivative crystallises from alcohol in pale-yellow needles, and melts at 103—104°. The corresponding 4-*ethoxy*-compound crystallises from alcohol in yellow needles and melts at 110—111°; the crystals are coloured red by concentrated sulphuric acid, and dissolve in it, yielding an orange-coloured solution. The *acetyl* derivative crystallises from alcohol in short, thick needles melting at 75°, and yields a *dibromide* which crystallises from a mixture of chloroform and ether in colourless needles melting at 130—131°. By the action of alcoholic potash, the dibromide is converted into 3-*ethoxy*-4′-*methoxyflavone*, $OEt\cdot C_6H_3\!<^{O-C\cdot C_6H_4\cdot OMe}_{\ \ CO\cdot CH}$; when purified by repeated crystallisation, this is obtained in colourless crystals melting at 144—145°, and gives an intense blue fluorescence with concentrated sulphuric acid; it is, however, somewhat difficult to free it from the isomeric coumaranone derivative which is produced in small quantities during the action. When boiled with an alcoholic solution of sodium ethoxide, it is decomposed in the normal way into 4-ethoxy-2-hydroxyacetophenone. If heated with concentrated hydriodic acid, it yields 3:4′-*dihydroxyflavone*, $HO\cdot C_6H_3\!<^{O-C\cdot C_6H_4\cdot OH}_{\ \ CO\cdot CH}$; this melts at 315°, and dissolves in caustic soda, forming a yellow solution with a pale-green fluorescence; its solution in sulphuric acid is colourless, but shows an intense blue fluorescence; the *diacetyl* derivative crystallises from alcohol in white, silky needles and melts at 182—183°. T. M. L.

Synthesis of 2-Hydroxyflavone. By STANISLAUS VON KOSTANECKI, R. LEVI, and J. TAMBOR (*Ber.*, 1899, **32**, 326—332).—*Quinacetophen-one monethylic ether* [5-*ethoxy*-2-*hydroxyacetophenone*], $OEt\cdot C_6H_3Ac\cdot OH$, crystallises from alcohol in yellow prisms and melts at 57°, whilst

2 : 5-*diethoxyacetophenone* crystallises in the triclinic system [$a : b : c$ = 0·8630 : 1 : 0·829; $\alpha = 87° 45'$, $\beta = 119° 15'$, $\gamma = 82° 45'$] and melts at 42°. By condensation with benzaldehyde, the latter substance gives 2 : 5-*diethoxyphenyl styryl ketone*, $C_6H_3(OEt)_2 \cdot CO \cdot CH:CHPh$, which crystallises from alcohol in yellow prisms, and melts at 50—51°. The monethylic ether, however, gives 2-*ethoxyflavanone*,

$$OEt \cdot C_6H_3 \diagdown \begin{matrix} O—CHPh \\ | \\ CO \cdot CH_2 \end{matrix}$$, which crystallises from alcohol in long,

glistening needles, melts at 103°, and shows a blue fluorescence in dilute alcoholic solution. By the action of bromine, it gives *bromo-2-ethoxyflavanone*, $OEt \cdot C_6H_3 \diagdown \begin{matrix} O \\ CO \end{matrix} \diagup C_2H_2BrPh$, which crystallises from alcohol in colourless flakes and melts at 98—99°. When treated with alcoholic potash, the bromo-compound loses a molecule of hydrogen bromide and gives 2-*ethoxyflavone*, $OEt \cdot C_6H_3 \diagdown \begin{matrix} O—CPh \\ || \\ CO \cdot CH \end{matrix}$; this crystal-

lises from alcohol and from light petroleum in needles, and from benzene in prisms, melts at 146—147°, and its solution in sulphuric acid shows a *green* fluorescence. It is decomposed in the normal way by sodium ethoxide, giving benzoic acid and 5-ethoxy-2-hydroxyaceto-phenone, whilst with hydriodic acid it gives 2-*hydroxyflavone*,

$$OH \cdot C_6H_3 \diagdown \begin{matrix} O—CPh \\ || \\ CO \cdot CH \end{matrix}$$; this crystallises from alcohol in colourless

needles, melts at 231—232°, shows a green fluorescence in sulphuric acid solution, and gives an *acetyl* derivative which crystallises in white, silky needles, and melts at 157—158°.   T. M. L.

Condensation of Nitrobenzaldehyde with Gallacetophenone. By HANS RUPE and J. LEONTÉEFF (*Chem. Centr.*, 1898, ii, 1043; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 390—391).—When a mixture of gallacetophenone (1 mol.) with meta- or para-nitrobenzaldehyde (1—2 mols.) and zinc chloride is heated at 90—100°, a compound, $NO_2 \cdot C_6H_4 \cdot CH[CH_2 \cdot CO \cdot C_6H_2(OH)_3]_2$, is obtained, which is not a deri-vative of triphenylmethane, as it is not oxidised by lead peroxide, and its colour reactions resemble those of gallacetophenone. The bases obtained by reducing this compound with stannous chloride yield azo-colours when diazotised and then condensed with phenols.   E. W. W.

Isomerides of the Rhodamines and the Pararhodamines. By EMILIO NOELTING and PAIRA (*Chem. Centr.*, 1898, ii, 1049; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 397—399).—The rhodamines ob-tained by the action of phthalic anhydride on dialkyl derivatives of orthamidophenols, must be regarded as orthocarboxyl derivatives of diamidophenylpyrone, in which the hydrogen atoms of the amido-groups are replaced by alkyl groups. The meta- and para-isomerides have been prepared by condensing nitrobenzaldehyde with dialkyl-metamidophenols, converting the triphenylmethane derivative,

$$NO_2 \cdot C_6H_4 \cdot CH[C_6H_3(OH) \cdot NR_2]_2,$$
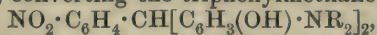
so obtained into a pyrone derivative, $NO_2 \cdot C_6H_4 \cdot CH \diagdown \begin{matrix} C_6H_3(NR_2) \\ C_6H_3(NR_2) \end{matrix} \diagup O$,

by eliminating water, then substituting carboxyl for the nitro-group,

and finally oxidising the leuco-base thus formed. These isomeric rhodamines have properties similar to those of ordinary rhodamines, and yield ethers corresponding with the anisolines.   E. W. W.

Meldola and Hughes' Perinaphthaquinone and Mono-bromindone. By CARL LIEBERMANN and S. SCHLOSSBERG (*Ber.*, 1899, **32**, 546—550).—The perinaphthaquinone described by Meldola and Hughes (*Trans.*, 1890, 393, 631, 808) as being formed by the action of nitric acid on dibromonaphthol is obtained in slightly better yield by using somewhat less nitric acid. It is found to be identical with the dinaphthaquinone, $C_{20}H_{10}O_4$, prepared by Witt and Dedichen (*Abstr.*, 1898, i, 144), since not only do the quinols and the acetyl derivatives of the quinols of both compounds agree in all their pro-perties, but also on distilling the perinaphthaquinone with zinc dust, Watson Smith's iso- (β-β ?)-dinaphthyl is produced. Probably also the dinaphthaquinone prepared by Staub and Watson Smith by oxidising isodinaphthyl is identical with this substance.

The chief product of the above reaction which Meldola and Hughes regarded as monobromindone, is in reality monobrom-α-naphtha-quinone, since, on bromination, it gives dibrom-α-naphthaquinone melt-ing at 218°, and not dibromindone, also, on treatment with ethylic sodiomalonate, it gives the blue coloration of halogenated α-naphtha-quinones and not the red colour which is characteristic of the chlorine and bromine derivatives of indone.   J. F. T.

The Naphthaquinone from Dibrom-α-Naphthol. By RAPHAEL MELDOLA (*Ber.*, 1899, **32**, 868—870. Compare Meldola, *Trans.*, 1890, **57**, 631).—The author's investigation of the perinaphthaquinone obtained from dibrom-α-naphthol by the action of fuming nitric acid has led to the result indicated by Liebermann and Schlossberg (fore-going abstract). The fact that this compound is a derivative of dinaphthyl is established by the action of hydroxylamine hydrochloride, which gives rise to the monoxime of a dinaphthylquinone.

The *oxime*, $C_{20}H_{10}O_3$:NOH, forms reddish-brown leaflets, and cannot be recrystallised from common solvents; it changes colour at 182—184°, but does not melt below 306°. It dissolves in dilute aqueous alkalis and alkali carbonates, yielding highly characteristic, blue solutions, from which acids precipitate the unaltered oxime; the blue colour of the alkaline solution changes to orange when zinc dust is added, being restored, however, on exposure to air. Concentrated sulphuric acid develops a green coloration which becomes violet on dilution.

The phenylhydrazone and anilide of the quinone have been prepared ; the *compound* with orthophenylenediamine crystallises from nitro-benzene in yellowish needles, and does not melt below 300°.

As regards the production of bromindone from dibrom-α-naphthol (*Trans.*, 1890, **57**, 393), the author states that the conditions peculiar to the original preparation of this compound have not been hitherto reproduced successfully.   M. O. F.

Synthesis of Hydroxyaldehydes of the Naphthalene Series. By LUDWIG GATTERMANN and TH. VON HORLACHER (*Ber.*, 1899, **32**, 284—286).—The hydroxy-derivatives of naphthalene yield aldehydes by

the method previously described (this vol., i, 363), with even greater ease than the monhydric phenols. 1 : 4-Hydroxynaphthaldehyde has already been described (Gattermann and Berchelmann, Abstr., 1898, i, 581) ; the *imide-hydrochloride*, $OH \cdot C_{10}H_6 \cdot CH : NH,HCl$, formed as an intermediate product in its preparation, is easily soluble in water and separates in colourless plates on adding ether to its solution in absolute alcohol. The *aniline* derivative, $C_{17}H_{13}NO$, of 1 : 4-hydroxy-naphthaldehyde, crystallises from dilute alcohol in lustrous, golden-yellow needles, and melts at 133° ; the *phenylhydrazone*, $C_{17}H_{14}N_2O$, separates from glacial acetic acid in yellow needles and melts at 119·5°.

The *imide-hydrochloride*, $C_{11}H_{10}NOCl$, derived from β-naphthol, forms colourless needles, and is easily converted by warm water into 2-hydroxy-1-naphthaldehyde, which melts at 81°, not at 76° as stated by Kaufmann (Abstr., 1882, 1068). The *azine*, $C_{22}H_{16}N_2O_2$, prepared from the latter, is very sparingly soluble in the usual solvents, and crystallises from nitrobenzene in golden-yellow needles which do not melt below 290° ; the condensation *product*, $C_{17}H_{13}NO$, which the aldehyde forms with aniline, crystallises from alcohol in yellow needles and melts at 93°, whilst the *phenylhydrazone*, $C_{17}H_{14}N_2O$, crystallises from acetic acid in golden plates, which darken and melt at 205°. W. A. D.

Colour Reactions of Indones and Quinones with Derivatives of Malonic Acid. By CARL LIEBERMANN (*Ber.*, 1899, **32**, 260—267. Compare this vol., i, 219).—*Bromindonemalononitrile*, $C_{12}H_5BrN_2O$, formed by the action of dibromindone on malononitrile in the presence of sodium ethoxide, crystallises in yellowish prisms melting at 139° ; it dyes wool reddish-brown. *Ethylic chlorindonemalonate*, $C_{16}H_{15}O_5Cl$, closely resembles the foregoing compound. *Ethylic brom-a-naphthaquinonemalonate*, $\dfrac{CO—CBr}{C_6H_4 \cdot CO} \!\!>\!\! C \cdot CH(COOEt)_2$, forms yellow crystals melting at 102°, and yields soluble blue alkali salts.

Ethylic brom-a-naphthaquinoneacetoacetate also forms yellow crystals and melts at 98°. When dibrom-a-naphthaquinone is treated in benzene solution with sodium ethoxide, *ethoxybrom-a-naphthaquinone*, melting at 118°, is formed together with the corresponding hydroxy-compound ; the ethoxy-derivative is also formed by the action of ethylic ethylmalonate on dibromonaphthaquinone, and, moreover, reacts with ethylic malonate in the same way as dibromonaphtha-quinone. *Ethylic bromo-β-naphthaquinonemalonate* crystallises in reddish-brown needles, melts at 96—97°, and forms a greenish-blue solution in alcoholic potash. *Ethylic 2-chlor-a-naphthaquinonemalonate* forms yellow crystals melting at 82—83°. Ethylic β-naphthaquinone-malonate crystallises in golden-brown needles melting at 107—108°.

The *anhydride* of *ethylic 3-acetamido-β-naphthaquinonemalonate*, $CO \!\!<\!\! \dfrac{CO—\!\!\overset{\|}{C} \cdot NAc—\!\!——}{C_6H_4 \cdot C \cdot CH(COOEt)} \!\!>\!\! CO$, formed by the action of ethylic sodio-malonate on chloracetamido-β-naphthaquinone, crystallises in reddish-brown needles which melt and decompose at 234°.

Bischlorindonephloroglucinol, $C_6H(OH)_3(C\underset{C_6H_4}{\overset{CCl-}{<}}>CO)_2$, is a red substance which decomposes and melts at 241°, and yields a blue solution in alcoholic sodium ethoxide.

In the preparation of these compounds, it is necessary to avoid an excess of alkali. The reaction only succeeds with quinones which possess a replaceable hydrogen or halogen atom. Benzylic cyanide and ethylic cyanacetate, and, occasionally, deoxybenzoin and acetyl-acetone react in a manner similar to that of ethylic malonate.

A. H.

Azo-dyes derived from 2′ : 1-Naphthylaminesulphonic Acid. By EMILIO NOELTING and BIANCHI (*Chem. Centr.*, 1898, ii, 1049—1050; from *Arch. Sci. phys. nat. Genève*, [iv], **6**, 399—400).—By the action of paranitrodiazobenzene in alkaline solution on 2′ : 1-naphthylamine-sulphonic acid, a *compound*, $SO_3H \cdot C_{10}H_6 \cdot NH \cdot N \dot{:} N_2 \cdot C_6H_4 \cdot NO_2$ [$SO_3H : NH = 1 : 2'$], is obtained, which has all the properties of a diazoamido-compound, and dyes silk and wool yellow. When the action takes place in an acid solution, however, an azo-compound, $SO_3H \cdot C_{10}H_5(NH_2) \cdot N_2 \cdot C_6H_4 \cdot NO_2$ [$SO_3H : NH_2 : N_2 = 1 : 2' : 1'$], is formed, which dyes wool purplish-red, and when reduced yields a naphthyl-enediaminesulphonic acid.

E. W. W.

Preparation of a Hydroxynaphthaquinonesulphonic Acid from Naphthol-yellow-S. By FRANZ GAESS (*Ber.*, 1899, **32**, 231—241).—Lauterbach has stated (Abstr., 1882, 63) that, on reduc-tion with tin and hydrochloric acid, naphthol-yellow-S (2 : 4-di-nitro-1 : 2′-naphtholsulphonic acid) gives rise to the double salt $[OH \cdot C_{10}H_4(NH_2)_2 \cdot SO_3]_2Sn, 2HCl, 4SnCl_2$; the diamido-acid is, how-ever, obtained free from tin when the reduction is carried out rapidly with little more than the theoretical amount of the metal, and a considerable excess of hydrochloric acid. 2 : 4-*Diamido*-1 : 2′-*naphthol-sulphonic acid* is, however, most conveniently prepared by shaking the dinitro-compound, in successive small quantities, with an aqueous solution of sodium hydrogen sulphite containing the zinc-dust theo-retically necessary to convert the latter into hyposulphite; on filtering the solution thus obtained into hydrochloric acid, the *hydrochloride*, $C_{10}H_{10}N_2SO_4, HCl$, separates in nearly colourless, rhombic plates. This is somewhat easily soluble in water, but is precipitated on adding hydrochloric acid; it dissolves in caustic soda, aqueous ammonia, and baryta-water, giving solutions which rapidly become red. When warmed with acetic anhydride and sodium acetate, it gives rise to *sodium triacetyldiamidonaphtholsulphonate*, which is insoluble in alcohol, but soluble in water; on adding barium chloride to the aqueous solution, the *salt*, $(C_{16}H_{15}N_2O_7S)_2Ba + 3\frac{1}{2}H_2O$, separates in white, stellar aggregates of needles, which are only sparingly soluble in cold water, but more readily in hot.

Amidonaphthaquinoneimidesulphonic acid (Lauterbach, *loc. cit.*) separates as a red, crystalline powder on blowing air through a cold ammoniacal solution of 2 : 4-diamido-1 : 2′-naphtholsulphonic acid, and in the form of lustrous scales on adding sodium nitrite to a solution

of the same substance in hydrochloric acid. It dissolves in concentrated sulphuric acid, but is precipitated unchanged on adding water; it does not form a compound with hydrogen chloride, but yields an *ammonium* salt in red crystals easily soluble in water, and a *barium* salt, $(C_{10}H_7N_2SO_4)_2Ba$, which is sparingly soluble in water, and forms microscopic, red leaflets. When amidonaphthaquinoneimidesulphonic acid is dissolved in 30 per cent. aqueous caustic soda, it gives rise initially to a separation of lustrous, golden needles, but after a time is decomposed with evolution of ammonia; when boiled during 7 hours with water, it is completely dissolved, and, on adding barium chloride, a crystalline precipitate of *barium hydroxynaphthaquinoneimidesulphonate* or *amidonaphthaquinonesulphonate*, $(C_{10}H_6NSO_5)_2Ba$, separates. On boiling amidonaphthaquinoneimidesulphonic acid with aqueous ammonia during 3 hours, and subsequently adding hydrochloric acid, a dark-coloured, crystalline powder having a slight metallic lustre is precipitated; this easily dissolves in water, and is oxidised by ferric chloride to a violet coloured acid-dye.

When ferric chloride is added to an aqueous solution of barium triacetyldiamidonaphtholsulphonate, acidified with acetic acid, *barium 2-acetamido*-1 : 4 : 2′-*naphthaquinonesulphonate*, $(C_{12}H_8NSO_6)_2Ba + \frac{1}{2}H_2O$, separates in golden needles; this is very sparingly soluble in water, but the corresponding *sodium* salt, $C_{12}H_8NSO_6Na + 3H_2O$, prepared similarly, readily dissolves in warm water, and crystallises in long, yellowish-red needles; in preparing these salts, isomerides do not appear to be formed. When the sodium salt is heated with aqueous caustic soda or with dilute hydrochloric acid, the acetamido-group is displaced by hydroxyl, 2-hydroxy-1 : 4 : 2′-naphthaquinonesulphonic acid (*infra*) being formed; when warmed with an aqueous solution of aniline acetate or hydrochloride, the *aniline* salt, $C_{18}H_{16}N_2SO_6 + 3H_2O$, separates in golden crystals, whilst orthophenylenediamine gives rise, under similar conditions, to the *salt*, $C_{16}H_{15}N_3SO_5 + H_2O$, derived from amidonaphthaquinonesulphonic acid; as eurhodine is not formed in the latter case, the acetamido-group in the original sodium salt must occupy position 2.

2-*Hydroxy*-1 : 4 : 2′-*naphthaquinonesulphonic acid* is formed when amidonaphthaquinoneimidesulphonic acid is boiled for 3 hours with dilute hydrochloric acid; the *normal barium* salt, $C_{10}H_4SO_6Ba + 3\frac{1}{2}H_2O$, separates in the form of long, yellowish-red needles when a similar decomposition is effected by boiling with baryta-water. The *barium hydrogen* salt, $(C_{10}H_5SO_6)_2Ba + 2H_2O$, separates from water in yellow needles, the *sodium hydrogen* salt, $C_{10}H_5SO_6Na + 3H_2O$, in bright-yellow six-sided plates, and the *normal sodium* salt, $C_{10}H_4SO_6Na_2$, in brownish-red crystals. When the sodium hydrogen salt is boiled with aniline in aqueous or alcoholic solution, it gives rise to the *aniline* salt, $C_{22}H_{18}N_2SO_5$, of an *anilidonaphthaquinonesulphonic acid*; this crystallises from water or dilute ammonia in beautiful, lustrous, crimson leaflets, and, when acted on by aqueous barium chloride, forms the red *barium* salt, $(C_{16}H_{10}NSO_5)_2Ba$, by the removal of aniline. When aqueous solutions of sodium hydroxynaphthaquinonesulphonate and orthophenylenediamine are mixed, and acetic acid subsequently added, orange-yellow crystals separate, which apparently consist

of the eurhodolesulphonic acid, $C_6H_4 <^{N=C\underline{\quad\quad}C\cdot CH:C\cdot SO_3H}_{NH\cdot C:CH\cdot CO\cdot C\cdot CH:CH}$;
this is almost insoluble in boiling water, but dissolves unchanged in
concentrated sulphuric acid, giving a crimson solution, and is not
decomposed when heated with concentrated hydrochloric acid during
several hours at 200°; it dissolves in aqueous caustic soda, yielding
the *sodium* salt, which forms red crystals, and is easily soluble in
water.   When aqueous solutions of phenylorthophenylenediamine
and sodium hydroxynaphthaquinonesulphonate are mixed in molecular
proportion, a brownish, crystalline precipitate is formed, which appar-
ently consists of 1 : 4 : 2 : 7-*rosindonesulphonic acid.*   W. A. D.

Oleum Cadi. By JULIUS TROEGER and P. FELDMANN (*Arch.
Pharm.*, 1898, **236**, 692—696).—The authors have attempted to
prepare cadinene from *Oleum cadi* according to Wallach's method, in
order to compare it with the oil obtained from the essential oil of
angostura bark (Beckurts and Troeger, this vol., i, 64); they find,
however, that the *Oleum cadi* examined by them contained very little
cadinene. The fraction boiling at 260—280° consisted of a mixture of
substances which could not be isolated in a pure form. An optically
inactive sesquiterpene, $C_{15}H_{24}$, boiling at 250—260° was obtained, but
it gave no solid derivatives with hydrogen chloride or hydrogen
bromide.   J. J. S.

**Extraction and Synthesis of the Odoriferous Principle of
Jasmine.** By ALBERT VERLEY (*Compt. rend.*, 1899, **128**, 314—317).
—By allowing repeatedly renewed jasmine blossoms to exhale their
perfume between sheets of glass coated with grease (*enfleurage à froid*)
and finally extracting the latter with vaseline oil, the fat remains un-
dissolved whilst the odoriferous principle is removed; this is then
isolated by shaking with acetone, evaporating the solution so obtained,
and fractionally distilling the product.   In this way, a light-yellow *oil*
is obtained which boils at 100—101° under 12 mm. pressure, possesses
an intense odour of jasmine, has a sp. gr. = 1·1292 at 0°, and, although
containing a small quantity of linalool, has a composition approximately
corresponding with that required for the formula $C_9H_{10}O_2$.   The oil, to
which the name *jasmal* is given, yields benzoic acid when oxidised
with chromic acid, the odour of formaldehyde becoming perceptible
during the process; when boiled with water (100 c.c.) containing
oxalic acid (1 gram) during several hours, it forms phenylglycol.
From these facts, it appears to consist of the *methylenic acetal*,
$^{CH_2-O}_{CHPh\cdot O}>CH_2$, of phenylglycol, and can be prepared synthetically
by warming the latter (50 grams) on the water-bath with water
(300 c.c.), sulphuric acid (125 grams), and formaldehyde (100 c.c.);
thus prepared, it boils at 101° under 12 mm. pressure, at 218° under
atmospheric pressure, has a sp. gr. = 1·1334 at 0°, and a refractive
index $\mu_D = 1·519$.
The corresponding *ethylidene* and *amylidene* acetals of phenylglycol
are prepared in the same manner and have similar properties; the

acetal, $\begin{array}{c} CH_2 \cdot O \\ | \\ CH_2 \cdot O \end{array}$>CHPh, prepared by Fischer and Giebe's method (Abstr., 1898, i, 167), boils at 140°.   W. A. D.

Ethereal Oil of Jasmine Flower. By ALBERT HESSE and FRIEDRICH MÜLLER (*Ber.*, 1899, **32**, 565—574).—As the result of a large number of experiments on the essential oil of the Jasmine flower, which Verley claims to have prepared synthetically by the condensation of phenylglycol and formaldehyde (preceding abstract), the authors are unable to understand how this investigator arrived at his conclusions. No trace of phenylglycol could be detected after heating the ethereal oil with oxalic acid, although this glycol is especially easy to isolate from its methyleneacetal. The essential oil contains no trace of phenylglycolmethyleneacetal, but consists of a mixture of ethylic benzylacetate and a salt of terpene alcohol, together with two other substances of unknown constitution to which this flower owes its characteristic smell. The formation of benzaldehyde, formaldehyde, and benzoic acid in Verley experiments was due to the ethylic benzylacetate.   J. F. T.

The Molecular Weight of Digitogenin and its Decomposition Products. By ALBERT EDINGER (*Ber.*, 1899, **32**, 339—341.)—The author has determined the molecular weights of digitonin, digitogenin and their oxidation products, digitogenic acid, hydrodigitoic acid, and digitic acid by the boiling point method, and finds them to be twice that indicated by the formulæ usually accepted; these must, therefore, be doubled, and the acids in question must be considered dibasic instead of monobasic.   J. F. T.

Anabsinthin. By ADRIAN and AUGUSTE TRILLAT (*Compt. rend.*, 1899, **128**, 115—117).—*Artemisia absinthium* contains a compound *anabsinithin*, $C_{18}H_{24}O_4$, soluble in alcohol, benzene, and chloroform, but only slightly soluble in water; this forms long, white, prismatic needles, which, when dried at 120°, melt at 258—259°; from acetone, it separates in large and peculiar crystals. With sulphuric acid, it gives a violet-red coloration that changes to blue, and with dilute hydrochloric acid (1 : 5), it gives a brown coloration and shows a slight green fluorescence when water is added. Acetic anhydride converts anabsinthin into a resin, but oxidising and reducing agents, and dilute acids and alkalis, have but little action on it. It does not reduce Fehling's solution, and yields no compound with phenylhydrazine. When distilled, it yields acetic and formic acids and an oil which becomes green and blue when exposed to air. Anabsinthin is quite distinct from the absinthin of Senger and of Bourcet.

                                              C. H. B.

Peucedanin and Oreoselone. By ERNST SCHMIDT, AUGUSTA JASSOY, and P. HAENSEL (*Arch. Pharm.*, 1898, **236**, 662—692. Compare Jassoy, Abstr., 1890, 1154 ; Popper, Abstr., 1898, i, 600).—Crude peucedanin has no definite melting point ; it is best purified by several extractions with warm ether, when a white, gritty residue is left ; when the ethereal solution is mixed with a considerable amount of light

petroleum, filtered, and left for a time, peucedanin is deposited in clusters of slender needles. After this process has been repeated several times, the compound is obtained in very slender, yellowish needles melting at 99°. It can be obtained perfectly colourless only by repeated recrystallisation from very dilute solutions; it then forms colourless, transparent prisms or plates, melting sharply at 109°. The melting point has been given very differently by different authorities. It is readily soluble in alcohol, ether, chloroform, acetone, sparingly in benzene or cold, light petroleum. Concentrated acids and alkalis decompose it, yielding oreoselone.

Analyses of the pure compound indicate that it has the composition $C_{15}H_{14}O_4$, and not $C_{16}H_{16}O_4$, and it is to be regarded as the methyl ether of oreoselone, since it contains one methoxy-group. Attempts to prepare peucedanin synthetically from oreoselone have proved unsuccessful.

A chloroform solution of peucedanin readily decolorises a chloroform solution of bromine, and a product is obtained which crystallises from ether in colourless, six-sided plates, melting at 140—141°. Bromine does not react so readily with oreoselone, but after chloroform solutions of the two have been allowed to remain for some time, a vigorous action sets in, and the same product, melting at 140—141° is obtained, namely, *monobromoreoselone*, $C_{14}H_{11}BrO_4$. Both compounds, when treated with nitric acid, yield nitroso-oreoselone crystallising in hexagonal prisms and pyramids, and melting at 171°. When reduced with tin and hydrochloric acid, the nitroso-compound yields hydroxylamine and oreoselone, and when treated with dry ammonia at 100°, a product is obtained melting at 156° (compare Bothe, *J. pr. Chem.*, 1849, **46**, 371). Oreoselone yields a *phenylhydrazone*, melting at 194°, and crystallising from alcohol in yellow plates; no phenylhydrazone has been obtained from peucedanin.

When treated with acetic anhydride and zinc chloride, peucedanin does not yield an acetyl derivative, whilst oreoselone, when treated with acetic chloride, yields the monacetyl derivative, melting at 123° (compare Popper (*loc. cit.*), and Hlasiwetz and Weidel, *Annalen*, 1874, **174**, 67).

Oxypeucedanin, $C_{30}H_{26}O_9$, obtained when the insoluble residue left in the purification of peucedanin, is dissolved in a small quantity of chloroform, and the solution mixed with an excess of ether, crystallises in colourless, strongly refractive, spindle-shaped crystals, resembling uric acid (compare Erdmann, *J. pr. Chem.*, 1838, **16**, 42, and Heut, *Annalen*, 1875, **176**, 70).   J. J. S.

Cheiranthin, an Active Constituent of the Wallflower. By MORITZ REEB (*Chem. Centr.*, 1898, ii, 1102; from *Arch. exp. Path. Pharm.*, **41**, 302—308).—Cheiranthin is obtained by evaporating the alcoholic or aqueous extract of the leaves or seeds of the wallflower, removing the inactive oils by light petroleum, treating with lead acetate, and finally salting out the glucoside with magnesium, sodium or ammonium sulphate, when it separates in small, yellow flakes, from which the salts may be removed by means of alcohol and ether. It may also be precipitated by tannin, and in either case still contains an

active alkaloid which may be removed by shaking with ether or ethylic acetate. Chieranthin brings about the characteristic systolic rest in frogs. E. W. W.

Aspidium spinulosum. By E. POULSSON (*Chem. Centr.*, 1898, ii, 1103—1104; from *Arch. exp. Path. Pharm.*, 41, 246—264).—The ethereal extract of the root of *Aspidium* or *Polystichum spinulosum* is evaporated, the residue ground up with calcined magnesia and extracted with water. The flesh-coloured precipitate obtained by adding sulphuric acid to the aqueous solution is dissolved in ether, and the ethereal solution dried over calcium chloride, when it yields a crystalline mass from which, by fractional crystallisation from alcohol, five different compounds may be separated. They are all insoluble in water, more or less soluble in ether, ethylic acetate, benzene, toluene, chloroform, and acetone, very slightly soluble in cold, but very soluble in warm methylic or ethylic alcohol, easily soluble in alkalis, and very slightly in alkaline carbonates; their alcoholic solutions are coloured red or brown by ferric chloride, and their solutions in concentrated sulphuric acid, on warming, become red, and acquire the odour of butyric acid. Their physiological action is like that of filicin.

Polystichin, $C_{22}H_{24}O_9$ (compare *Arch. exp. Path. Pharm.*, 35, 97), in alcoholic solution has a feeble acid action on litmus, gives an intense garnet-red coloration with ferric chloride, reduces ammoniacal silver solution, but has no action on Fehling's solution. *Polystichin-aniline*, $C_{22}H_{24}O_9, C_6H_7N$, forms rhombic crystals and melts at 132°.

Polystichalbin, $C_{22}H_{26}O_9$, melts at 150—150·5°, crystallises from acetone in small needles spherically arranged, and from alcohol in small, white needles. The alcoholic solution has an acid re-action, and gives a brownish-yellow coloration with ferric chloride. The compound with aniline, $C_{22}H_{26}O_9, 2C_6H_7N$, melts at 175°, that with phenylhydrazine, $C_{22}H_{26}O_9, 2C_6H_8N_2$, separates from alcohol in small, yellow crystals, and melts at 179°. Polystichinin, $C_{18}H_{22}O_8$, crystallises from acetone in lustrous, colourless plates, and from ethylic acetate in plates 2—3 cm. long and 0·5 cm. broad; it dissolves in dilute sodium carbonate solution without liberating gas, and the solution becomes deep Burgundy red after several hours. It reduces ammoniacal silver solutions in the cold, but Fehling's solution only on prolonged boiling. The alcoholic solution is feebly acid, and with ferric chloride gives a dark brown coloration. *Polystichocitrin*, $C_{15}H_{22}O_9$, crystallises from methylic alcohol in small, lustrous, yellow leaflets, and from alcohol in matted needles; its alcoholic solution is neutral to litmus, and with ferric chloride gives a brownish coloration; its compound with aniline, $C_{15}H_{22}O_9, C_6H_7N$, forms small, yellow prisms and melts at 117—118°. *Polystichoflavin*, $C_{24}H_{30}O_{11}$, which crystallises in long, yellow needles often grouped in star-shaped clusters, melts at 158—158·5°; the alcoholic solution is acid to litmus, and is coloured brown by ferric chloride.

By the action of dilute sodium hydroxide solution and zinc dust on polystichin, polystichic acid, polystichinol, a phenol which melts at 120—121°, and butyric acid are formed. Polystichic acid (Abstr., 1896, i, 387) separates from alcohol in small, lustrous crystals, is very soluble

in alcohol, rather soluble in hot water, dissolves in sodium carbonate solution without liberating carbonic anhydride, has a strong acid reaction, gives a faint yellowish-brown with ferric chloride, and a yellow coloration with aniline ; its solution in warm concentrated sulphuric acid has the odour of butyric acid. *Polystichinol*, $C_{21}H_{30}O_9$, crystallises from ether in yellow prisms, and from alcohol in slender, pale yellow needles ; it melts at $156.7°$, is very slightly soluble in cold ether, but easily so in hot ether and in benzene ; its alcoholic solution is acid to litmus, and gives a reddish-brown coloration with ferric chloride. In doses of 10 milligrams, polystichic acid and polystichinol have no action on frogs.   E. W. W.

Cantharidin. II. Isomerides of Cantharidin. By HANS MEYER (*Monatsh.*, 1898, **19**, 707—726. Compare Abstr., 1898, i, 43). —Cantharic acid, prepared by the action of chlorosulphonic acid on cantharidin, has the molecular weight corresponding with that required for the formula $C_{10}H_{12}O_4$, as determined by the boiling point method, using acetone as solvent. The existence of a stable γ-lactone ring in cantharic acid is shown by the fact that, whereas only one equivalent of potash is required to neutralise the acid in the cold, 50 per cent. more is required when the acid is boiled with aqueous potash, a certain proportion of the dipotassium salt being then present in solution. The amount of hydrogen sulphide liberated from a solution of potassium hydrosulphide is also nearly double that calculated for one carboxyl group. Cantharic acid, unlike cantharidic acid, is readily oxidised by alkaline potassium permanganate, but the products of the reaction have not yet been identified. These reactions agree with the constitution $\begin{matrix} C_7H_{10} \\ | \\ CO \cdot O \end{matrix}\rangle CH \cdot COOH$.

Isocantharidin, $C_7H_{10}\underset{CO-O}{\overset{CH(OH)}{<}}>CO$, which was obtained by Anderlini and Ghiro (Abstr., 1891, 1243), has the same molecular weight as cantharidin, and requires 2 mols. of potash for its neutralisation in boiling solution. When boiled with barium acetate, a barium isocantharidate is produced which, when decomposed by sulphuric acid, yields isocantharidic acid, $COOH \cdot C_7H_{10} \cdot CH(OH) \cdot COOH$; this has the normal molecular weight and is not converted into an anhydride by adding acetic anhydride to its solution in aqueous sodium carbonate, a reaction which confirms the view that it is a derivative of glutaric acid. Isocantharidic acid must be regarded as a hydrate of cantharic acid, and this view is supported by the fact that it is converted into cantharic acid by long continued boiling with water.

                                                A. H.

Samandarin. By EDWIN S. FAUST (*Chem. Centr.*, 1898, ii, 1213—1214 ; from *Arch. exp. Path. Pharm.*, **41**, 229—245).—By extracting 200 earth salamanders (*Salamandra maculosa*) with hot water acidified with acetic acid, treating with lead acetate, and precipitating with phosphotungstic acid, the author obtained a solution containing only a small quantity of Zuleski's samandarin. The solution is alkaline, gives precipitates with several alkaloidal reagents, but does not yield crystalline salts. With auric chloride, it becomes turbid ,

and the chloride is reduced on warming; with platinic chloride, it gives an amorphous, reddish-brown, and, with bromine water, a yellowish-white, precipitate soluble in hot water. When evaporated with nitric acid, the solution leaves a yellow stain which, with ammonia, gives a yellowish-red, and with sodium hydroxide solution, a red coloration. Physiologically, samandarin affects the nervous system, acting on the nerve centres in the *medulla oblongata*, especially on that connected with the respiratory organs; it causes convulsions, like picrotoxin, &c., and also tetanic spasms.　　　　E. W. W.

Chemistry of Chlorophyll. By LEON MARCHLEWSKI (*J. pr. Chem.*, 1899, [ii], 59, 22—29).—A continuation of the controversy with Bode (Abstr., 1898, i, 682).　　　　C. F. B.

Chlorophylls. By ALEXANDRE ÉTARD (*Ann. Chim. Phys.*, 1898, [vii], 13, 556—574. Compare Abstr., 1895, i, 66, 389; 1897, i, 578, ii, 130, and this vol., i, 46).—This paper contains an account of the method employed in extracting the chlorophylls from lucerne (*Medicago sativa*). The greater portion refers to work already published, and the remainder to general considerations unsuitable for abstraction.

　　　　G. T. M.

Brazilin and Hæmatoxylin. IV. By JOSEF HERZIG (*Monatsh.*, 1898, 19, 738—746. Compare Abstr., 1893, i, 426; 1894, i, 341; 1896, i, 379).—Carefully purified brazilin yields both resorcinol and protocatechuic acid on fusion with potash, and must therefore be a derivative of β-resorcylic acid. The fact that the colour of alkaline solutions of brazilin is not due to this substance, is proved by the observation that an alkaline solution which has been rendered perfectly colourless by reduction with hydroxylamine, still yields pure brazilin on acidification. The colour usually seen is due to brazilein. Dimethylbrazilein could only be obtained as a syrup insoluble in alkalis; its *acetyl* derivative is an amorphous substance melting at 150—155°. Acetylbrazilein appears from its properties to be a true brazilein derivative, and not to belong to the brazilin series, as is supposed by Schall and Dralle (Abstr., 1890, 997). Moreover, the product obtained by reducing brazilein with various reducing agents is not identical with brazilin, although its exact nature has not yet been ascertained. All these facts seem to show that brazilein cannot be the quinone of brazilin (compare also Gilbody and Perkin, Proc., 1899, 15, 27, 75).　　　　A. H.

Lichens and their Characteristic Constituents. By OSWALD HESSE (*J. pr. Chem.*, 1898, [ii], 58, 465—561. Compare Abstr., 1898, i, 531, 679).—Under each lichen is given the locality where it was found, and the substances obtained from it.

Thamnolia vermicularis (Sw.), from the Cavalljoch, Vorarlberg.—Thamnolic acid, melting at 210—211° (Zopf, 202—204°, Abstr., 1893, i, 727).

Cladonia rangiferina (L.) *vulgaris* (Schaerer) = *C. rangiferina* (Leighton), from Feuerbach near Stuttgart, and from the Starnberger See.—Atranorin and protocetraric acid.

C. rangiferina (L.) *silvatica* (Hoffm.) = *C. silvatica* (Nylander), from

between Schloss Solitude and Leonberg (near Feuerbach?), and from the Starnberger See.—Usnic and protocetraric acids, but not cetraric acid, as Zopf asserts.

C. Floerkeana Fr. = *C. bacillaris* Ach., from the neighbourhood of Feuerbach.—Coccellic acid (Abstr., 1895, i, 299; 1898, i, 489).

Parmelia tiliacea (Hoffm.) Fr. = *Imbricaria tiliacea* Körber, from Ehingen, and from Brand (Vorarlberg).—Atranorin and lecanoric acid; the latter was mistaken by Zopf for a new substance, and named parmelialic acid.

P. fuliginosa Nylander, from Brand, and from Heiden (Switzerland).—Atranorin and lecanoric acid.

Physcia pulverulenta (Schreber) Nyl. (a)-*allochroa* (Hoffm.) Th. Fr., from the neighbourhood of Schloss Solitude.—A very small quantity of an acid which was not obtained crystallised.

P. ciliaris (L.) D. C. = *Anaptychia ciliaris* Körber, from Schloss Solitude.—Everninic acid, and probably atranorin; it is probable that the former was not originally present in the lichen, but was formed from evernic or ramalic acid under atmospheric influence.

Umbilicaria pustulata(L.)Hoffmann = *Gyrophora pustulata* Ach., from Weissenstein near Pforzheim, and from St. Blasien (Black Forest).— Gyrophoric acid, $C_{18}H_{18}O_7$ (?) (Stenhouse, *Annalen*, 70, 218; Zopf, Abstr., 1898, i, 489); when this is boiled with ethylic alcohol, ethylic orsellate is formed, together with an *acid* melting at 163°, which gives a violet and yellowish-red coloration with ferric chloride and bleaching-powder solutions respectively, and is not orsellic acid, as Zopf asserts.

Gyrophora polyphylla (L.) Fro. = *Umbilicaria polyphylla* Fr.—Umbilicaric acid, melting and decomposing at 180° (Zopf, Abstr., 1898, i, 489).

Endocarpon miniatum (L.) Ach., (a) *vulgare* Körber, and (β) *complicatum* (Sw.) Fr., from Brand.—Phytosterol (observed in a lichen for the first time) and an *acid* which gives a bluish-violet coloration with alcoholic ferric chloride.

Placodium saxicolum (Poll.) var. *vulgare* Kbr., from Feuerbach.— Usnic acid and zeorin (Paternò, *Atti R. Accad. Lincei*, 1876, [ii], 3; Zopf, Abstr., 1896, i, 104), but not atranorin, as Zopf asserts. Usnic acid is best separated from atranorin by pounding the mixture with concentrated aqueous potassium hydrogen carbonate, filtering, and extracting the residue with chloroform, which dissolves out the atranorin, leaving the potassium usneate behind. Zeorin melts at 230—231°, and has the molecular formula $C_{52}H_{88}O_4$; when it is boiled with alcohol and a little hydrochloric acid, it yields zeorinin, $C_{52}H_{84}O_2$, and an amorphous isomeride, *isozeorin*, more soluble in alcohol; these melt at 182—184° and 184—185° respectively; the former crystallises anhydrous from absolute alcohol, with $2H_2O$ from aqueous alcohol, and is converted into the isomeride by alcoholic hydrochloric acid.

Blastenia arenaria, Massalongo = *Callopisma erythrocarpa* (Pers.) de Not., from Feuerbach.—Phytosterol (?) and *blastenin*, an orange-red substance melting at 270°, soluble in aqueous potassium hydrogen carbonate, and apparently related to nephromin.

B. arenaria (Pers.) var. *teicholytum* Ach. = *Callopisma teicholytum*

Ach., from Feuerbach.—Atranorin and an acid apparently identical with gyrophoric acid.

Lecanora sordida (Pers.), Th. Fr., var. *glaucoma* (Hoffm.), from Feuerbach.—Atranorin and parellic acid, but neither zeorin, nor sordidic nor usnic acid. Zopf's zeoric acid (Abstr., 1897, i, 436) was probably impure parellic acid.

L. sordida (Pers.), Th. Fr., var. *Swartzii* (Ach.), from Feuerbach.— From the ethereal extract, atranorin and thiophanic acid crystallise out on cooling; the latter can be removed by extraction with a dilute aqueous alkali hydrogen carbonate. From the ethereal mother liquor, aqueous potassium hydrogen carbonate extracts roccellic and lecasteric acids, of which the latter is the more soluble in chloroform or acetic acid, and its barium salt the more soluble in water. When the residual ethereal solution is evaporated, atranorin and lecasteride remain; the latter can be dissolved out with a little hot alcohol.

Thiophanic acid, $C_{12}H_6O_{12}$, which crystallises from benzene anhydrous, and from acetic acid with $1H_2O$, is yellow and melts at $242°$; it loses carbonic anhydride when fused with caustic potash, but not when boiled with aqueous baryta, does not contain a methoxyl group and does not form an acetyl derivative. It is a dibasic acid; the following salts were analysed: $C_{12}H_4O_{12}K_2 + 4H_2O$, yellow; $C_{12}H_4O_{12}Ba + 5H_2O$, yellow; $C_{12}H_4O_{12}Pb + H_2O$ (dried at $110°$). When the acid is boiled with hydriodic acid of sp. gr. $= 1.7$, yellow *thiophaninic acid*, $C_{12}H_6O_9 + H_2O$, melting at about $264°$, is formed. *Lecasteride*, $C_{10}H_{18}O_3$, melts at $105°$; it is converted into lecasteric acid by alkalis and alkali carbonates, and is formed when that acid is boiled with acetic anhydride. *Lecasteric acid*, $C_{10}H_{20}O_4$, melts at $116°$; it does not contain methoxyl, and is a monobasic acid; the anhydrous *barium*, *silver*, and *ethylic* salts were analysed. Roccellic acid melted at $127—128°$; the *barium* salt, $C_{17}H_{30}O_4Ba$, was analysed.

Urceolaria scruposa (L.), var. *vulgaris* Körber, from Feuerbach.— Atranorin and lecanoric acid.

U. cretacea Massalongo = *U. scruposa*, var. *gypsacea* Körber, from Brand.—Lecanoric acid alone, but not atranorin, zeorin, or parmelialic acid, as Zopf asserts (Abstr., 1897, i, 436).

Pertusaria communis (DC.) *β-variolosa* Wallr. = *P. amara* = *Variolaria amara*, from Feuerbach and Schloss Solitude.—From the ethereal extract, potassium hydrogen carbonate solution removes cetraric and pertusaric acids; these can be separated by means of the greater solubility of the latter in dilute alcohol. The residual ethereal solution yields a crystalline residue, which is washed with warm alcohol to remove the resinous mother liquor, and then crystallised from hot chloroform, when pertusarin remains dissolved on cooling, whilst pertusarene and pertusaridin separate; of these, the former can be separated by adding light petroleum to a solution of the mixture in hot chloroform. *Pertusaric acid*, $C_{24}H_{38}O_6$ (or $C_{23}H_{36}O_6$), melts at $103°$, and has no bitter taste when pure; the *silver* salt, $C_{24}H_{37}O_6Ag$, was analysed. *Pertusarin*, $C_{30}H_{50}O_2$, melts at $235°$, *pertusarene*, $C_{60}H_{100}$, at $286°$; and *pertusaridin*, which has some resemblance to caperidin, at $242°$. None of these substances gives a coloration with ferric chloride or bleaching powder. No picrolichenin could be

detected; perhaps the substance described under this name (Alms, *Annalen*, 1, 61; Vogel, *J. pr. Chem.*, [i], 72, 272) was impure per-tusaric acid.

Thallœdema candidum (Webr.) Körber, from Brand.—Traces of an *acid*, perhaps lecanoric acid.

Baeomyces roseus (Pers.) from Stockheim (Wurtemberg) and Brand.—In addition to wax, it contains an *acid* which melts at about 180° and gives a violet coloration with ferric chloride.

Lecidea cineroatra Ach., from Brand.—From the ethereal extract, potassium hydrogen carbonate solution removes lecidic acid and lecidol, which can be separated by means of the greater solubility of the latter in dilute alcohol. *Lecidic acid*, $C_{22}H_{27}O_4 \cdot COOMe$, melts at 147°, and contains either one or two COOH groups in addition to the COOMe group. *Lecidol*, melts at 93°, and has the character of a phenol; the pure substance is not soluble in potassium hydrogen carbonate solution.

Rhizocarpon geographicum (L.) DC. *f. lecanorinum* (Flörke) and *f. geronticum* Ach., from Baden, the Luisenberg and the Arber (Böhmer-wald), the Achensee (Tyrol), and Brand.—From the ethereal solution, aqueous potassium hydrogen carbonate extracts parellic acid: also, rhizocarpinic acid, in the case of the lichen from the Luisenberg and probably in the other cases; the latter acid is extracted from the mixture by cold alcohol. The residual ethereal solution yields rhizo-carpic acid when evaporated. *Rhizocarpic acid*, $COOH \cdot C_{24}H_{16}O_3 \cdot COOEt$, is yellow, and melts at 177—178°; its *potassium* salt, with $1H_2O$, is yellow, and insoluble in aqueous potassium hydrogen carbonate; when it is evaporated repeatedly with potassium carbonate, it yields *nor-rhizocarpic acid*, $C_{24}H_{16}O_3(COOH)_2$; this acid is yellow and melts at 92°; the *potassium* salt, with $5H_2O$, is also yellow; and so is the *diethylic* salt, which is obtained by boiling rhizocarpic acid with alcohol and a little hydrochloric acid, and melts at 159°. When rhizocarpic acid is warmed for 6 hours with acetic anhydride at 85° and the mixture evaporated, a yellow *monacetyl* derivative, melting at 168°, is obtained; if it is boiled with the anhydride, pulvic anhy-dride is formed; some ethylpulvic acid is formed when it is boiled for a short time with aqueous baryta. *Rhizocarpinic* acid is yellow and melts at 156°. Parellic acid (identical with Zopf's psoromic acid, Abstr., 1895, i, 298; 1897, i, 363; and the squamaric acid, and, probably, zeoric acid of other writers), $COOMe \cdot C_{17}H_{11}O_3(COOH)_2$, crystallises from glacial acetic acid with $3H_2O$, from moderately dilute alcohol with $1H_2O$; the anhydrous acid melts and decomposes at 262—265°. It is a dibasic acid, and contains one methoxyl group; it yields neither an ethylic salt nor an acetyl derivative; the following *salts* were analysed, $2C_{21}H_{14}O_9Pb,PbO$ (with H_2O in addition, if dried in a desiccator only); $C_{21}H_{14}O_9Ag_2$; $C_{21}H_{15}O_9Ag$. When the acid is boiled with aqueous baryta or potassium carbonate, it loses carbonic anhydride and methylic alcohol, and yields *parellinic acid*, $C_{17}H_{14}O_4(COOH)_2$, which melts and decomposes at 230°; it is a dibasic acid; the yellow barium salt, with $6H_2O$, was analysed.

Rhizocarpon geographicum (L.) DC. *f. contiguum* Fr., from Brand.—When the ethereal extract was shaken with potassium hydrogen

carbonate solution, the potassium salts of parellic and rhizonic acids separate out, whilst rhizocarpic acid remains dissolved; of the two salts, the first dissolves in cold water, the latter does not (perhaps it could be used for the separation of potassium and sodium, as the sodium salt is soluble in water). Calcium oxalate is also present in the lichen. *Rhizonic acid*, $OMe \cdot C_{17}H_{14}O_2(OH)_2 \cdot COOH$, melts and decomposes at 185°; the *barium*, with $3H_2O$, *copper*, with 3 or $4H_2O$, and anhydrous *potassium*, *calcium*, *lead*, and *silver* salts were analysed. When it is heated with hydriodic acid, betorcinol is formed, together with methylic iodide and carbonic anhydride; the same products are also obtained when the acid is boiled with aqueous baryta, but some *rhizoninic acid*, $OMe \cdot C_6HMe_2(OH) \cdot COOH$, is also formed; this melts at 186°, and, like rhizonic acid, yields betorcinol, methylic iodide and carbonic anhydride, when it is heated with concentrated hydriodic acid; its *potassium*, with $1H_2O$, *barium*, with $3H_2O$, and *copper*, with $3H_2O$, salts were analysed, and a crystalline *ethylic* salt was prepared. Rhizonic acid is a lactonic acid; it is related to rhizoninic acid in the same way as evernic to everninic acids, and the first pair is derived from betorcinol in the same way as the second pair from orcinol.

Calycium chrysocephalum Ach. = *Cyphelium chrysocephalum*, Ach., from Feuerbach and Munich.—Vulpic acid only.

Cyphelium trichiale f. candelare, Arnold, from Munich.—Calycin.

Lepra candelaris Schaerer = *Lepraria flava* Acharius, from Feuerbach, the Black Forest, Salzburg, and on cinchona bark from Bolivia, India, Ceylon, and Java.—Calycin, $C_{18}H_{11}O_4 \cdot OH$, melts at 240—242°; it yields a purple-red *potassium* derivative, with $2H_2O$, when treated with alcoholic potash or concentrated aqueous potassium carbonate; this decomposes into calycin and potassium calycate, $C_{18}H_{12}O_6K_2$, when it is boiled with water. When calycin is heated for several hours at 100° with caustic potash of sp. gr. = 1·15°, crystals are obtained which melt at 195°, and are possibly oxatoluic acid. When 40 per cent. potash is used and the heating continued for 1 hour at 100° and then for 1 hour at 150°, the products are oxalic and α-toluic acids, with possibly a little toluene. Calycin yields a yellow *acetyl* derivative, melting at 178°. It was not found possible to convert calycin into vulpic (methylpulvic) acid, although it is undoubtedly related to pulvic acid.

Pulveraria chlorina Ach. = *Lepra chlorina* Stenh., from St. Anton (Tyrol).—Calycin remains in the ethereal extract, whilst potassium hydrogen carbonate removes vulpic and lepraric acids from the ether; these were separated by crystallisation from acetone. *Lepraric acid* melts at 228°, and does not give any coloration with ferric chloride or bleaching powder.

P. latebrarum = *Lepra latebrarum* Ach., from Brand.—From the ethereal extract, atranorin separates on cooling. Potassium hydrogen carbonate solution removes parellic acid. The residual ethereal solution yields atranorin, latebride, and pulverin; of these, the last two can be dissolved out with dilute alcohol and separated by means of the greater solubility of latebride in chloroform. *Latebride* melts at 128°; it forms, with concentrated potash, a gelatinous precipitate, but this dissolves after a time, and an acid, *latebraric acid*, can then be

isolated from the solution. *Pulverin* is pale yellow; it melts and decomposes at 262°.

P. farinosa Ach.—From the ethereal extract, potassium hydrogen carbonate removes oxyroccellic and pulveraric acids; the first of these forms an insoluble, the latter a soluble barium salt. *Pulveraric acid* melts at 234°, and gives a blue coloration with ferric chloride.

Cetraria islandica (L.) Ach. (compare Abstr., 1898, i, 534, and Sinnhold, this vol., i, 13).—Samples purchased from Frankfort and Stuttgart, and one collected near Wunsiedel (Fichtelgebirge) contain a lichenostearic acid, or acids, with melting points ranging between 109—120°, and composition between C 69·1—70·0, H 9·5—9·9. From a second sample purchased from Frankfort, a small quantity of another acid, *paralichenostearic acid*, was isolated in addition; this melts at 183°, and has the composition C 67·6, H 10·0.

As regards the occurrence, in lichens generally, of the substances described, it cannot be said that a particular constituent is characteristic of a particular lichen; it often occurs in other, and by no means closely related, lichens as well. The season of the year has some, but not a great influence in determining what constituents are present: *Cladonia rangiferina* var. *silvatica* contains fatty acids in summer, but not in winter. The nature of the material upon which the lichen grows has more influence: *Parmelia caperata* contains caperin and caperidin when it has grown on oaks, but not when it has grown on fruit trees or on granite; and *Xanthoria parietina* usually contains physcion, but this is absent when the lichen has grown on pines, and atranorin is present instead, and the colour is now greenish instead of yellow. Climate has a great influence: *Parmelia perlata* from Germany contains atranorin only, whereas that from America contains vulpic and usnic acids, and that from India perlatin and lecanoric acid, in addition. The use of chemical tests to distinguish species of lichens is not admissible, as different parts of the same lichen may react differently.   C. F. B.

Constitution of Indican and of some Derivatives of Indigotin. By LEON MARCHLEWSKI and L. G. RADCLIFFE (*J. Soc. Chem. Ind.*, 1898, **17**, 430—434).—The constitution suggested for glucosides (Abstr., 1894, i, 104), namely, $OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CH{<}^{CH \cdot OR}_{O}$, in which R represents a phenolic or basic residue, is considered preferable to the one previously suggested (Trans., 1893, 1137). Acetochlorhydrose is constituted in much the same manner as a glucoside, and should therefore be either $OAc \cdot CH_2 \cdot CH(OAc) \cdot CH{<}^{[CH \cdot OAc]_2}_{O}{>}CHCl$, or $OAc \cdot CH_2 \cdot [CH \cdot OAc]_3 \cdot CH{<}^{CHCl}_{O}$. As galactose cannot be found among the products of hydrolysis, the second formula is considered the more probable.

In view of Schunck and Römer's work (*Ber.*, 1879, **12**, 2311), indican cannot be regarded as the glucoside of indigo white; it cannot contain the whole indigotin molecule in any form, and indigotin is produced by condensation going on under favourable conditions simul-

taneously with the hydrolysis of indican. The constitution now suggested
for indigotin, $OH \cdot CH_2 \cdot [CH \cdot OH] \cdot _3 \cdot CH \underset{O}{\overset{CH \cdot O \cdot C:CH}{<}} \overset{}{\underset{C_6H_4}{}} > NH$, repre-
sents it as the glucoside of indoxyl.

The acid obtained by O'Neill (Abstr., 1892, 991) on oxidising indigo
suspended in glacial acetic acid and hydrolysing the product, is shown
to have the composition $C_{16}H_{14}N_2O_6$, when air dried, and is termed
di-isatic acid; it contains water of crystallisation, softens at 140—149°,
but melts at 226—227°. When dried at 110—115° it loses $2H_2O$,
yielding an anhydrous acid, *di-isatin*, $C_{16}H_{20}N_2O_4$; this is a white
powder readily soluble in methylic or ethylic alcohol, or acetone, but
insoluble in chloroform, carbon bisulphide, or ether. Titration with
standard alkali indicates that the composition of its *sodium* salt is
$C_{16}H_9NaN_2O_4$, and that of the hydrated acid $C_{16}H_{13}NaN_2O_6$. A *bromo-*
derivative of the hydrated acid, namely, $C_{16}H_{12}Br_2N_2O_6$, has been
obtained as a white powder which slowly melts and decomposes.

From a study of the behaviour of natural and artificial indigos on
oxidation, it would seem that the two are identical; indirubin, on the
other hand, differs from indigo on oxidation. Although indirubin is
readily reduced to indigotin in the presence of acid reducing agents,
the reduction does not proceed so readily when alkaline reducing
agents are employed. J. J. S.

Action of Ethylenic Iodide on Pyridine. By ALBERT LADEN-
BURG (*Ber.*, 1899, 32, 42—46. Compare Abstr., 1883, 1151).—
Pyridine (5·5 grams) was heated with di-iodethane (16 grams) and
absolute alcohol (about 2 grams) at 310—320° for 10 hours, the opera-
tion being repeated 180 times in all, and the united product submitted
to repeated fractional distillation; the products were (*a*) pyridine,
boiling at 115—120°; (*b*) 2-ethylpyridine, boiling at 146—153°,
and yielding picolinic acid on oxidation (the *mercurochloride*,
$C_5NH_4Et, HCl, 2HgCl_2$, melts at 103—106°); and (*c*) 4-ethylpyridine,
boiling at 160—168°, and giving isonicotinic acid when oxidised.
Probably the ethylenic iodide does not act directly on the pyridine, but
decomposes, yielding hydrogen iodide, which then reacts with the
alcohol present to form ethylic iodide, the ethylpyridines being pro-
duced by the action of the pyridine on the latter. C. F. B.

New Organo-metallic compounds. By FRITZ BLAU (*Monatsh.*,
1898, 19, 647—689).—*aa*-Dipyridyl combines with ferrous salts,
forming stable, deep red tridipyridylferrous salts of the general
formula $(C_{10}H_8N_2)_3FeR_2$; these are characterised by specific reactions
entirely different from those of ferrous salts, and are only very slowly
decomposed by acids and by ammonium sulphide. The soluble com-
pounds dye silk and wool pink. *Tridipyridylferrous sulphate*, formed
when dipyridyl is added to an aqueous solution of ferrous sulphate, is
a deep red, crystalline mass which is extremely soluble in water. The
other salts are best prepared from this compound by double decomposi-
tion; the sulphate and nitrate are readily soluble, the chloride,
bromide, and iodide less readily, and the others insoluble, or spar-
ingly soluble, in water. The *iodide*, with $5H_2O$ or $8H_2O$, and the

bromide crystallise in dark-red, lustrous, six-sided tablets; the *platino-chloride*, $(C_{10}H_8N_2)_3FePtCl_6 + 5\frac{1}{2}H_2O$, forms brownish-red, crystalline aggregates. The *base*, $(C_{10}H_8N_2)_3Fe(OH)_2$ is formed when baryta is added to the sulphate, and is a red, strongly alkaline substance which combines with atmospheric carbonic anhydride, and readily decomposes, forming ferric hydroxide. The formation of these compounds proceeds even in acid solution, and the coloration which is produced may be used as a test for dipyridyl. Similar compounds are formed with salts of zinc, cadmium, nickel, cobalt, and copper, but not with salts of the alkali metals, alkaline earth metals, lead, manganese or aluminium. The red salts are not affected by atmospheric oxygen, or by oxidising agents of moderate strength, but are converted by potassium permanganate, nitric acid, and chlorine water, into *tridipyridylpseudoferric salts*, $(C_{10}H_8N_2)_3FeR_3$ which form blue solutions in water; these compounds are not formed when dipyridyl is added to ferric salts. They are very readily reconverted into the original red salts by reducing agents, such as hydrogen sulphide, metallic silver, hydrobromic acid, hydrogen peroxide, and also by exposure to light. Acids do not cause decomposition when the possibility of reduction is excluded; alkalis render the blue solutions red, a smell of ozone being produced, but on acidifying, the blue colour returns. The *sulphate* has not been obtained in the pure state, but the *platinochloride* is a well characterised compound, $(C_{10}H_8N_2)_6Fe_2(PtCl_6)_3$, which crystallises with 19 or $20H_2O$, in slender, green needles, the anhydrous compound being brown.

Tridipyridylnickel salts, which are formed in a similar manner to the ferrous salts, are pink; the *bromide*, $(C_{10}H_8N_2)_3NiBr_2 + 6\frac{1}{2}H_2O$, crystallises in six-sided tablets, and the other salts resemble it in appearance. Tridipyridylcobalt salts form brownish-yellow solutions; the *bromide* crystallises in yellow, six-sided tablets, and dissolves in about 100 parts of water. Two series of copper salts are known, produced by the union of 1 mol. of copper salt with 1 or 2 mols. of the base. *Dipyridylcopper sulphate*, $C_{10}H_8N_2,CuSO_4 + 2H_2O$, crystallises in sparingly soluble, blue needles, and the *chloride* forms compact green crystals readily soluble in water; the compounds containing 2 mols. of the base are very unstable. Dipyridyl also forms colourless compounds with the salts of zinc and cadmium; these are sparingly soluble in water. Compounds also seem to be formed with chromic and ferric salts, but no definite results have as yet been obtained.

The isomerides of αα-dipyridyl do not form similar compounds, and in this respect resemble aniline, naphthylamine, the phenylenediamines, benzidine, &c. One or two direct derivatives of αα-dipyridyl, however, behave somewhat similarly, and a series of similar compounds has been obtained from the *α-phenanthroline* prepared from orthophenylenediamine; this compound crystallises with $1H_2O$ in vitreous, hexagonal plates melting at 102°, whilst the anhydrous compound melts at 117°. The *platinochloride* crystallises in microscopic prisms, and the *dichromate* in sparingly soluble needles; the metallic compounds of this base closely resemble those of dipyridyl in almost every respect. *Triphenanthrolineferrous sulphate*, prepared by adding the base to ferrous sulphate solution, serves as a source of the

other compounds; the *bromide*, $(C_{12}H_8N_2)_3FeBr_2 + 7H_2O$ crystallises in red, quadratic prisms. The ferrous salts are converted by oxidation into blue pseudo-ferric compounds; *triphenanthrolinepseudoferric platinochloride*, $(C_{12}H_8N_2)_6Fe_2(PtCl_6)_3$, crystallises in green needles, which yield an olive-green residue of anhydrous salt when dried over sulphuric acid. *Triphenanthrolinenickel bromide* forms pink tablets, whilst the corresponding *cobalt* compound crystallises in yellow needles. The compounds with copper, zinc, and cadmium salts, closely resemble those of dipyridyl.

The constitution of these compounds appears to be best explained by Werner's theory of the metalammines, according to which they must be classed as hexammines (luteo-salts), all the acid radicles being capable of entering into double decompositions. A. H.

A Di-iodoquinoline. By CONSTANTIN I. ISTRATI (*Compt. rend.*, 1898, **127**, 520—521).—The method employed by the author for the iodation of benzene and its chlorine derivatives, and for the preparation of franceines, which consists in prolonged heating of the substance with concentrated sulphuric acid and iodine, is found to be generally applicable to cyclic nitrogen compounds. In the case of quinoline, much sulphurous anhydride is evolved, the mixture thickens and becomes of a reddish-brown or black colour, and on pouring the mass into water a precipitate is produced which consists of iodoquinolines and iodofranceines, whilst moniodoquinoline, sulphonic derivatives, and unaltered quinoline remain in solution. By treating the precipitate with potash, filtering, and exhausting the insoluble residue with alcohol, a *di-iodoquinoline*, $C_9NH_5I_2$, is obtained, which forms yellowish-brown crystals melting at 164—165°. It is very soluble in alcohol and chloroform, and forms a yellow *platinochloride* and other salts, which are decomposed by excess of water. The moniodoquinoline crystallises from alcohol in small, colourless needles melting at 101—102°, and is, perhaps, identical with the 5-iodoquinoline described by Claus and Grau (Abstr., 1893, i, 669) as melting at 100°. Its platinochloride, however, does not melt and decompose at 263°, as stated by those observers, and is separable by treatment with hot water, into two portions: the one, soluble in water, crystallises in orange-yellow needles, which lose iodine at 210°, and melt and decompose at 228°, whilst the other, insoluble in water, is of a golden-yellow colour, and melts and decomposes at 230—260°. N. L.

Condensation Products of Formaldehyde with Quinaldine. By WILHELM KOENIGS (*Ber.*, 1899, **32**, 223—231. Compare this vol., i, 74).—Quinaldine combines not only with 1 mol. of formaldehyde, as Methner has stated, but also with 2 and 3 mols., forming α-quinolyl-propanediol and α-quinolylbutanetriol, respectively.

α-Quinolylethanol [2-hydroxyethylquinoline], $C_9NH_6 \cdot CH_2 \cdot CH_2 \cdot OH$, which was described under the name of quinaldinealkin by Methner (Abstr., 1895, i, 71), crystallises from ethylic acetate in colourless, hexagonal plates melting at 104—105° (94—95° Methner); the *picrate* crystallises from water in yellow needles melting and decomposing at 165°, the aurichloride forms glistening, yellow scales melting at 132—135°, and the platinochloride separates from hot dilute

hydrochloric acid in yellowish-red plates melting and decomposing at 210°.

a-Quinolylpropanediol, $C_9NH_6 \cdot CH(CH_2 \cdot OH)_2$, formed by heating a mixture of quinaldine and formaldehyde in a sealed tube for 40 hours in a water-bath, crystallises from ethylic acetate or from hot water in colourless prisms which melt at 116—117°, and are readily soluble in ethylic and methylic alcohol, methylal, acetone, and chloroform, sparingly in cold ethylic acetate and in benzene, and almost insoluble in ether, carbon bisulphide, and light petroleum; the *picrate* melts at 146—147°; the *aurichloride*, when first formed, is an oil, but solidifies on standing, and the *platinochloride*, after drying at 130°, melts and decomposes at 155—160°. a-Quinolylpropandiol, on reduction with phosphorus and hydriodic acid, yields 2'-isopropylquinoline, which is identical in every respect with the compound obtained by Doebner (Abstr., 1887, i, 504) from a-isopropylcinchonic acid, and yields an *aurichloride* melting at 124—126°, and a *platinochloride* melting at 194°.

a-Quinolylbutanetriol, $C_9NH_6 \cdot C(CH_2 \cdot OH)_3$, formed from quinaldine and 3 mols. of formaldehyde, crystallises from ethylic acetate or benzene, and melts at 143°; the *hydrochloride* melts at 143—146°, the *platinochloride* is readily soluble, and the *aurichloride*, which crystallises in glistening, yellow leaflets containing $1H_2O$, melts at 86°, or when anhydrous, at 122—123°; on oxidation with nitric acid, the base yields quinoline-2'-carboxylic acid, and on reduction with phosphorus and hydriodic acid, not tertiarybutylquinoline, but a-isopropylquinoline, which seems to point to this compound as being in reality a-quinolylpropanediol containing formaldehyde of crystallisation; the author is disinclined to this belief, however, owing to the fact that not only does a-quinolylbutanetriol yield no compound with phenylhydrazine, but also that a-quinolylpropanediol may be boiled for a prolonged period with formaldehyde without change; further, the base does not react with Tollen's reagent for formaldehyde.   J. F. T.

Synthesis of Pyridazine and its Derivatives. By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1899, **32**, 395—409).—When benzoylacrylic acid (von Pechmann, Abstr., 1882, 1074) is warmed with an aqueous solution of hydrazine, it gives rise to the *hydrazone*, $N_2H_3 \cdot CPh \cdot CH \overset{..}{\cdot} CH \cdot COOH$, which separates from absolute alcohol in slender, colourless crystals, melts and decomposes at 185—186°, and is not convertible into 3-phenylpyridazone by the loss of $1H_2O$. Benzoylpropionic acid, however, like its ethylic and methylic salts (Curtius, Abstr., 1895, i, 246; von Rothenburg, *ibid.*, 302), when acted on by hydrazine, gives rise to phenylpyridazinone, $\begin{smallmatrix} CPh \cdot CH_2 \cdot CH_2 \\ || \quad\quad\quad | \\ N—NH—CO \end{smallmatrix}$; on dissolving this (70 grams) in glacial acetic acid (200 c.c.) and adding bromine (65 grams), it is converted into a *bromophenylpyridazinone*, which loses hydrogen bromide when crystallised from alcohol, and gives rise to 3-*phenylpyridazone*, $\begin{smallmatrix} CPh \cdot CH \overset{..}{\cdot} CH \\ || \quad\quad\quad | \\ N—NH—CO \end{smallmatrix}$, melting at 201—202°. On warming the latter with phosphorus oxychloride, it yields 3-*phenyl-*

6-*chloropyridazine*, $\begin{array}{c} CPh{\cdot}CH{:}CH \\ \| \qquad | \\ N{-}N{=}CCl \end{array}$, which crystallises from alcohol in long, colourless prisms, and melts at 160°; it is converted by sodium methoxide into 3-*phenyl*-6-*methoxypyridazine*, which crystallises from alcohol in fan-shaped aggregates of needles, melts at 116—117°, and yields well-defined *compounds* with hydrogen chloride, potassium dichromate, picric acid, and gold and platinum chlorides. On boiling 3-phenyl-6-chloropyridazine for 2 hours with concentrated hydriodic acid (b. p. 127°) in presence of red phosphorus, it is converted into 3-*phenyl*-6-*iodopyridazine*, $C_{10}H_7N_2I$, which crystallises from absolute alcohol in snow-white needles, and, when heated, sinters at 163°, and melts at 169—170°; when, however, the boiling is continued for 5 hours, 3-*phenylpyridazine*, $\begin{array}{c} CPh{\cdot}CH{:}CH \\ \| \qquad | \\ N{-}N{=}CH \end{array}$, is obtained, which crystallises from water or light petroleum in long needles, melts at 102—103°, boils unchanged at 330—332°, sublimes slightly at 100°, and has an odour resembling that of diphenyl. The *hydriodide*, $C_{10}H_8N_2,HI$, forms yellow prisms, and the *platinochloride*, $(C_{10}H_8N_2)_2,H_2PtCl_6$, very slender needles, whilst the golden-yellow, crystalline *aurichloride*, $C_{10}H_8N_2,HAuCl_4$, melts at 159°, and the *picrate* at 127°.

When 3-phenylpyridazine is reduced with alcohol and sodium, and the product dissolved in dilute nitric acid, *phenylhexahydropyridazine nitrate*, $\begin{array}{c} CHPh{\cdot}CH_2{\cdot}CH_2 \\ | \qquad\qquad | \\ NH{-}NH{-}CH_2 \end{array},HNO_3$, is obtained, which forms thick, colourless needles, and, when heated, sinters at 179°, and melts at 187°; the *base* is an oil, whilst the *picrate*, $C_{10}H_{14}N_2,C_6H_3N_3O_7$, forms yellow prisms and melts at 170—171°. On nitration, 3-phenylpyridazine gives rise to a mixture of isomeric *nitro*-derivatives, $C_{10}H_7N_3O_2$, which seem to crystallise together from water, since the crystals commence to melt at 151° and finally liquefy at 195°; when reduced, an *amidophenylpyridazine*, $C_{10}H_9N_3$, is obtained, which crystallises from dilute alcohol in rhombic plates, softens at 110°, melts at 120—124°, and is converted by the diazo-reaction into a *hydroxyphenylpyridazine*, $C_{10}H_8N_2O$; this, when heated, softens at 170°, melts at 177—180°, and is not identical with that described below.

Paramethoxybenzoylpropionic acid, $OEt{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, prepared by adding powdered aluminium chloride (15 grams) to succinic anhydride (10 grams) dissolved in phenetoil, crystallises from alcohol in flat, rhombic plates, and melts at 138—139°; analogy with Nourrisson's results (Abstr., 1886, 1029) in the case of anisoil and phthalic anhydride indicates that the ethoxy-group is in the para-position. When hydrazine sulphate is added to a solution of the acid in excess of caustic soda, *paraphenetylpyridazinone*, $OEt{\cdot}C_6H_4{\cdot}C{\Large\lessgtr}{\begin{array}{c} CH_2{\cdot}CH_2 \\ N{-}NH \end{array}}{\Large\gtrless}CO$, is obtained, which forms long needles, and melts at 145—146°. When this is treated with bromine (1 mol.) in glacial acetic acid solution, it gives rise to a *monobromo*-derivative, $C_{12}H_{11}N_2BrO_2$, which separates in beautiful, transparent rhombs, and melts at 240—243°; 3-*bromophenetyl*-6-*chloropyridazine*, $OEt{\cdot}C_6H_3Br{\cdot}C{\Large\lessgtr}{\begin{array}{c} CH{:}CH \\ N{-}N \end{array}}{\Large\gtrless}CCl$, prepared

from it by the action of phosphorus oxychloride, crystallises from alcohol in colourless needles, melts at 152—153°, and is converted by boiling hydriodic acid (b. p. 127°) into *3-parahydroxyphenylpyridazine*, $OH \cdot C_6H_4 \cdot C \underset{N——N}{\overset{CH:CH}{<\quad>}} CH$, which dissolves sparingly in water, but easily in alcohol. It is readily oxidised by cold aqueous potassium permanganate to *pyridazine-3-carboxylic acid*, $COOH \cdot C \underset{N——N}{\overset{CH:CH}{<\quad>}} CH$, which crystallises from water in needles or plates, melts at 200—201°, and yields a crystalline *hydrochloride*, *aurichloride*, and *platinochloride*; the *copper* salt, $(C_5H_3N_2O_2)_2Cu$, crystallises from water in bright blue rhombs. Pyridazine, obtained on distilling the carboxylic acid, has a sp. gr. = 1·1108 at 18·1°, referred to water at 16·5°, and possesses the properties ascribed to it by Täuber (Abstr., 1895, i, 301); its *picrate*, $C_4H_4N_2,C_6H_3N_3O_7$, forms citron-yellow needles which sinter at 160° and melt and decompose at 175°.   W. A. D.

Synthesis of Pyridazone-derivatives. By Augústin Bistrzycki and Hŭgo Simonis (*Ber.*, 1899, **32**, 534—536).—The aliphatic 1 : 4-aldehyde-acid, mucobromic acid, like the aromatic orthaldehyde-acids, shows a tendency to pass into ring compounds by the condensation of its side chains.

When mucobromic acid, in alcoholic solution, is boiled with phenylhydrazine, a mixture of the phenylhydrazone and its inner anhydride is formed; this can be separated by means of dilute sodium hydroxide solution.

Mucobromic acid phenylhydrazone, $N_2HPh:CH \cdot CBr:CBr \cdot COOH$, is difficult to obtain pure, since, on acidifying the sodium hydroxide solution, it does not separate unchanged; crystals which had been mechanically separated from the original mixture melted at 105—110°.

Phenyldibromopyridazone, $CH \underset{N——NPh}{\overset{CBr:CBr}{<\quad>}} CO$, the inner anhydride, is, however, readily obtained pure, and crystallises from alcohol in glistening, colourless, truncated prisms, melting at 145°; it is insoluble in water, dilute aqueous potash, or diluted mineral acids, but readily soluble in glacial acetic acid or toluene.

Dibromopyridazone, $CH \underset{N——NH}{\overset{CBr:CBr}{<\quad>}} CO$, separates as a crystalline precipitate when an aqueous solution of mucobromic acid, hydrazine sulphate, and sodium acetate is boiled; it crystallises from alcohol in colourless needles, melting at 224°, and is readily soluble in warm dilute sodium hydroxide solution. On adding baryta to the pyridazone, the *barium* salt separates in white needles containing $1\frac{1}{2}H_2O$; this it loses on drying at 110°, becoming at the same time coloured an intense yellow.   J. F. T.

1 : 9-Dimethyluric Acid and 1 : 7 : 9-Trimethyluric Acid. By Emil Fischer and Friedrich Ach (*Ber.*, 1899, **32**, 250—260).—The following experiments were undertaken with the object of preparing 1 : 9-dimethyl- and 1 : 7 : 9-trimethyl-uric acid, and thus completing the list of the possible di- and tri-methyl derivatives of uric

acid. 2-Chloro-6-amido-8-oxy-9-methylpurine (Abstr., 1898, i, 280), is converted by nitrous acid into 2-*chloro*-6 : 8-*dioxy*-9-*methylpurine*,

$$\begin{matrix} NH \cdot CO \cdot C \cdot NH \\ | \quad\quad || \\ CCl : N \cdot C \cdot NMe \end{matrix} \Big> CO,$$ which crystallises in long matted needles, and

melts and decomposes at about 320° (corr.) ; this, when treated with ammonia, yields the corresponding *amido*-compound, from which a large amount of guanidine can be obtained on oxidation. Chlorodioxy-methylpurine, on reduction with hydriodic acid and phosphonium iodide

at 60°, yields 6 : 8-*dioxy*-9-*methylpurine*, $$\begin{matrix} NH \cdot CO \cdot C \cdot NH \\ | \quad\quad || \\ CH : N \cdot C \cdot NMe \end{matrix} \Big> CO,$$ which

crystallises from hot alcohol in short, compact prisms, and becomes brown at 390° without melting. Chlorodioxy-9-methylpurine readily reacts with methylic iodide in alkaline solution, forming 2-*chloro*-6 : 8-*dioxy*-1 : 7 : 9-*trimethylpurine*, $C_8H_9N_4O_2Cl$, which crystallises in slender needles melting at 258—259° (corr.). The chlorodioxy-9-methyl-purine is converted by a smaller amount of methylic iodide into

2-*chloro*-6 : 8-*dioxy*-7 : 9-*dimethylpurine*, $$\begin{matrix} NH \cdot CO \cdot C \cdot NMe \\ | \quad\quad || \\ CCl : N \cdot C \cdot NMe \end{matrix} \Big> CO,$$ which

is also formed by the action of dilute alkalis on 2 : 6-dichloro-8-oxy-7 : 9-dimethylpurine; it separates from acetic acid in granular crystals and melts at 312° (corr.). 2-Chloro-6 : 8-dioxy-1 : 7 : 9-trimethyl-purine is readily converted by heating with hydrochloric acid into

1 : 7 : 9-*trimethyluric acid*, $$\begin{matrix} NMe \cdot CO \cdot C \cdot NMe \\ | \quad\quad || \\ CO \cdot NH \cdot C \cdot NMe \end{matrix} \Big> CO,$$ which crystallises

from alcohol or water in lustrous needles and melts and decomposes at 348° (corr.) ; this acid closely resembles hydroxycaffeine in its proper-ties, but is less stable than the latter, and does not give so marked a murexide reaction. The *silver* salt crystallises in slender, matted needles soluble in ammonia.

2-*Chloro*-6 : 8-*dioxy*-1 : 9-*dimethylpurine* is prepared by acting on 2-chloro-6 : 8-dioxy-9-methylpurine with formaldehyde, treating the potassium salt of the hydroxymethyl derivative thus formed with methylic iodide, and hydrolysing the product. It crystallises in lustrous needles and melts and decomposes at 291° (corr.). This compound is converted by reduction into 6 : 8-*dioxy*-1 : 9-*dimethyl-purine*, which forms concentric groups of small needles, and melts at 360—362° (corr.). When heated with hydrochloric acid, it yields 1 : 9

dimethyluric acid, $$\begin{matrix} NMe \cdot CO \cdot C \cdot NH \\ | \quad\quad || \\ CO - NH \cdot C \cdot NMe \end{matrix} \Big> CO,$$ which crystallises in rect

angular tablets, is soluble in 360 parts of boiling water, decomposes at about 400°, and reduces ammoniacal silver oxide solution when boiled with it. The *sodium* salt is precipitated by concentrated aqueous soda in fascicular groups of needles ; the *potassium* salt crystallises in very slender needles. A. H.

The Purine group. By EMIL FISCHER (*Ber.*, 1899, **32**, 267—273). —When treated with alcoholic ammonia at 100°, trichloro-9-methyl-purine is converted into dichloro-9-methyladenine, and a com-pound $C_6H_5N_5Cl_2$, which melts and decomposes at 314°, and is probably the isomeric 2 : 6-*dichloro*-8-*amido*-9-*methylpurine*.

The α-dimethyluric acid described by Mabery and Hill (Abstr., 1879, 48), is formed by methylating pure lead 3-methylurate, prepared from 3-methylchloroxanthine. As the dimethyluric acid is converted by hydrochloric acid and potassium chlorate into methylcarbamide and methylalloxan, it follows that it is a 3 : 9-derivative.

3 : 9-Dimethyluric acid yields a considerable amount of 2 : 6-dichloro-8-oxy-9-methylpurine when treated with phosphorus oxychloride and pentachloride, the methyl group in position 3 being removed. This explains the fact that a crude methyluric acid, containing both 3- and 9-methyluric acids, as well as 3 : 9-dimethyluric acid, yields more of the 9-methylpurine derivative than corresponds with the amount of the 9-methyluric acid present.

7-Methyluric acid is converted by phosphorus oxychloride into 2 : 6-dichloro-8-oxy-7-methylpurine, and this, when treated with phosphorus pentachloride, yields 7-methyltrichloropurine ; if, however, the oxy-compound is heated with excess of phosphorus oxychloride at 150—160°, it yields a compound, $C_{10}H_7N_6OCl_3$, which crystallises in slender, colourless needles, melts at 281° (corr.), is decomposed by alkalis, and on treatment with hydriodic acid yields 8-oxy-7-methyl-purine. A. H.

Solubility of Coniine in Carbon Bisulphide. By HERM. MELZER (*Arch. Pharm.*, 1898, **236**, 701—703).—According to Blyth (*Annalen*, 1849, **70**, 77), coniine is but sparingly soluble in carbon bisulphide, but according to the author, this alkaloid readily combines with it, yielding *coniine coniylthiocarbamate*, $C_3H_7 \cdot C_5H_9NH, C_3H_7 \cdot C_5H_9N \cdot CS \cdot SH$. This is best obtained by mixing ethereal solutions of the two constituents in equivalent quantities, evaporating the ether under diminished pressure, and crystallising the residue from light petroleum ; it forms colourless needles melting at 71—72°, and is readily soluble in all the ordinary solvents.

When hydrogen sulphide is passed into a dry ethereal solution of coniine, crystalline needles are deposited, but rapidly deliquesce when exposed to the air. J. J. S.

Triacetylmorphine and the Oxidation of Morphine. By HENRI CAUSSE (*Compt. rend.*, 1899, **128**, 181—183).—Ten grams of morphine are dissolved in 150 grams of acetic anhydride, 10 grams of dry and fused sodium acetate, and 10 grams of zinc powder are added, and the mixture is boiled in a reflux apparatus until all the zinc has dissolved. After cooling, the crystalline mass is suspended in acetic anhydride, the liquid drained off, distilled, the residue purified in the usual way, and finally crystallised from methylic alcohol. The *triacetylmorphine*, $C_{23}H_{27}NO_6 + H_2O$, obtained in this way loses its water of hydration at 115° ; the hydrate melts at 155° and the anhydrous salt at 158°, which is lower than the melting point of either the mono- or di-acetyl derivatives. Triacetylmorphine is soluble in methylic or ethylic alcohol, but insoluble in cold solutions of caustic alkalis or alkali carbonates ; it gives no coloration with ferric chloride, selenious anhydride or nitric acid. Its salts are very soluble and crystallise with difficulty, but the oxalate can be obtained in silky crystals. The formation of a tri-acetyl derivative under the conditions described may be attributed to

reduction of the carbonyl group CO to COH by the hydrogen resulting from the action of the zinc on the acetic acid formed.

When morphine is dissolved in acetic acid and boiled with iodic acid in an atmosphere of oxygen, it loses one molecular proportion of carbonic anhydride for each molecular proportion of morphine.

From these facts, it follows that the third oxygen atom exists in the morphine as a carbonyl group CO, this group and two hydroxyl groups being directly united with the nitrogen. C. H. B.

Precipitates in Extr. Fluid. Hydrastis. By OTTO LINDE (*Arch. Pharm.*, 1898, **236**, 698—701. Compare Schmidt and Kerstein, Abstr., 1890, 649).—The precipitates formed after some time in liquid extracts of *Hydrastis* differ in composition. The chief constituents are usually berberine and hydrastine, and sometimes small quantities of phytosterol. The amount of hydrastine is small when its slight solubility in alcohol is considered. J. J. S.

Is Hydrastine Free or Combined in Hydrastis Rhizome and in the Liquid Extract? By OTTO LINDE (*Arch. Pharm.*, 1898, **236**, 696—698).—According to Dohme and Engelhardt (*Pharm. Rund.*, 1895, 235), part of the hydrastine in *Hydrastis* rhizome is present in the free form and part in the form of salts. Determinations made by the author indicate that there is no definite numerical relationship between the free and combined hydrastine. J. J. S.

Hyoscyamus Muticus. By JOHANNES GADAMER (*Arch. Pharm.*, 1898, **236**, 704. Compare Dunstan and Brown, Trans., 1899, 72).— The chief alkaloid of Egyptian *Hyoscyamus muticus* is hyoscyamine. Scopolamine has not been found, but small quantities of atropine have been isolated. J. J. S.

Epinephrine. By JOHN J. ABEL (*Proc. Amer. Physiol. Soc.*, 1898, 3—4, 4—5. *Amer. J. Physiol.*, 2).—*Epinephrine*, the active material of suprarenal capsules, can be separated from aqueous extracts as a benzoate. It is alkaloidal in nature, and has the formula $C_{17}H_{15}NO_4$. Various salts were prepared, but most of these are inactive; the chemical operations involved reduce their activity. If the benzoate is decomposed in an autoclave in the presence of a 1 or 2 per cent. solution of sulphuric acid, at a pressure of from 3 to 5 atmospheres, intensely active solutions are obtained. The picrate prepared from the benzoate by direct precipitation with sodium picrate is also active, although it is contaminated with a picrate of unknown composition, but containing a high percentage of nitrogen. The sulphate is also active. The benzoate loses acetic acid on drying. W. D. H.

Cynarasin. By GIOVANNI EMILIO RASETTI (*L'Orosi*, 1898, **21**, 289—302).—An aqueous infusion of the flowers of the wild artichoke (*Cynara cardunculus, L.*) is used instead of rennet in the manufacture of a certain kind of Italian cheese, and the author describes a number of experiments which prove that the coagulating power of the infusion is due to the presence therein of a soluble ferment, since it is not affected by the addition of antiseptics and is due neither to the

natural acidity of the liquid nor to micro-organisms. A temperature of about 50° is most favourable to the action of the ferment, whilst coagulation is altogether prevented by heating above 65°. The ferment, for which the name *cynarasin* is proposed, is precipitated, on adding alcohol to its solution, as a brown, amorphous powder, soluble in water. The aqueous solution is neutral, does not coagulate on heating, froths strongly on agitation, gives no coloration with tincture of guaiacum, gives a brown precipitate with basic lead acetate, is rendered slightly turbid by acetic acid and potassium ferrocyanide, and rather more turbid by nitric acid, picric acid, and the chlorides of mercury, gold, and platinum. Cynarasin is capable of coagulating 150,000 times its weight of milk, but has no action on starch or albumin ; it contains carbon, hydrogen, oxygen, and nitrogen (7·17 per cent.), but neither sulphur nor phosphorus.   N. L.

Products of the Digestion of Albumin. II. Isolation of the so-called Carbohydrate Group of Egg-albumin. By SIGMUND FRÄNKEL (*Monatsh.*, 1898, **19**, 747—769).—When egg-albumin, carefully freed from globulin and ovomucoid, is heated with aqueous baryta, a compound is produced in small quantity which is a snow-white, non-hygroscopic, indistinctly crystalline powder, becomes brown at 160° and decomposes at 200° without melting. It is readily soluble in water, sparingly in alcohol, gives a very intense reaction with α-naphthol and sulphuric acid, and does not reduce Fehling's solution, or give the biuret reaction. It gives no red coloration with phloroglucinol and hydrochloric acid, and does not yield furfuraldehyde when distilled with phosphoric acid. After boiling with dilute acids, it yields a substance capable of reducing Fehling's solution and forming an *osazone* melting at 204°. This substance, for which the author proposes the name *albamine*, has the composition $2(C_6H_9O_4 \cdot NH_2) + H_2O$, and is dextrorotatory, $a_D = 30 \cdot 22°$; with benzoic chloride, it yields a crystalline derivative which melts at 195°, and thus resembles glucosamine in many respects, being most probably either identical or isomeric with it. A similar product has been obtained from egg-albumin by digestion with pepsin and hydrochloric acid, and also by digestion with trypsin.

The sugar produced from albumin in cases of diabetes, is probably derived from a much more complete disintegration of the albumin molecule than that represented by the formation of albamine, as the yield of this substance is insufficient to account for the amount of sugar excreted by diabetic patients.   A. H.

Melanins. By WALTER JONES (*Proc. Amer. Physiol. Soc.*, 1898, 6 ; *Amer. J. Physiol.*, 2).—A black pigment, which does not contain sulphur, was obtained from a hydrochloric acid extract of horse hair. By oxidation in an alkaline medium, carbonic anhydride and ammonia are obtained; in an acid medium, intermediate products, namely, a substance resembling putrescin, and a light-yellow pigment, $C_{18}H_{11}N_5O_{10}$, are also obtained.   W. D. H.

Organic Chemistry.

Explosibility of Acetylene at Low Temperatures. By GEORGES CLAUDE (*Compt. rend.*, 1899, **128**, 303—304).—Under atmospheric pressure and at − 80°, acetone dissolves more than 2000 times its volume of acetylene. Explosion does not occur on immersing in the solution a platinum wire heated to redness by an electric current, although Berthelot and Vieille have stated that a similar cause readily brings about an explosion in the case of a solution of the gas prepared at the ordinary temperature under a pressure of 20 atmospheres. Liquid acetylene at − 80°, under a pressure of 1·3 atmospheres, is not exploded by a heated wire, so that under these conditions the gas can be liquefied without danger. W. A. D.

Action of Sulphuric Acid on Acetylene. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, **128**, 333—339).—The potassium salt of the acid derived from the action of sulphuric acid on acetylene, previously described (this vol., i, 264), has the composition $3C_2H_2,4KHSO_4$. Ordinary sulphuric acid absorbs only a small quantity of acetylene, but the product yields a minute quantity of phenol when heated with potassium hydroxide at 250°. A similar result is obtained when the fuming acid acts on aldehyde or paraldehyde.

Acetylene hydrate is formed in very small quantity when the gas is absorbed by fuming sulphuric acid, but the yield is larger with the ordinary acid and still larger with the acid $H_2SO_4 + H_2O$. If the product from the monohydrate is diluted with water and distilled, it yields crotonaldehyde mixed with either ethylenic glycol or "vinylic alcohol." When the distillate is treated with silver oxide and the insoluble products containing excess of silver oxide are treated with hydrogen sulphide, a thio-acid, most probably thioglycollic or thiohydroxyglycollic acid, is formed. C. H. B.

Action of Chlorine on Chloroform and Bromine on Bromoform in Presence of the Corresponding Aluminium Halogen Salts. By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, **19**, [iii], 179—180).—In the methane series, the aluminium compound has practically no effect in promoting further substitution. In the higher series, this agent first induces the formation of unsaturated compounds with which the halogen forms additive products. G. T. M.

Decomposition of Iodoform by Light. By EDWARD KREMERS and E. C. W. KOSKE (*Pharm. Archives*, 1898, **1**, 194—200).—The decomposition of iodoform by light does not reach a limit as Fleury states (*J. Pharm.*, [vi], **6**, 97), but is dependent on the amount of iodoform, the length of exposure, and, above all, on the nature of the light—whether direct sunlight or indirect, that is, light which has passed through a solution of iodine in potassium iodide. By exposing an alcoholic solution of iodoform to direct sunlight for 30 minutes 1·9—2·12 per cent. of the iodine contained in the iodoform was

liberated, in 1 hour 2·87—3·23, and in 3 hours 4·86—5·51. Indirect exposure, however, only caused a liberation of 0·386—0·503 per cent. in 30 minutes, 0·353—0·806 in 1 hour, and 0·416—1·14 in 2 hours. When iodine has been liberated and dissolved, the colour of the solution largely protects the rest of the iodoform from decomposition, by absorbing the actinic rays, but Fleury's proof of this is invalid, for when an alcoholic solution of iodoform containing precipitated metallic silver was placed in the dark for 3 days, 80·4 per cent. of the iodine was obtained as silver iodide, after 4 days 81, and after 7 days 98·1 per cent.   E. W. W.

Chemical Behaviour of Iodoform, and its Detection in Aqueous Solutions. By LUDWIG VON STUBENRAUCH (*Chem. Centr.*, 1898, ii, 1285; from *Zeit. Unters. Nahr.-Genussm.*, 1898, 737—741).—Iodoform acts on concentrated solutions of silver nitrate, forming carbonic oxide, nitric acid, and silver iodide, and when triturated with silver nitrate, it decomposes with explosive violence, forming dense fumes of iodine, silver iodide, nitrogen oxides, and probably carbonic oxide. When iodoform is suspended in water and exposed to sunlight, free iodine and probably also hydrogen iodide are formed and dissolved. If iodoform suspended in water is warmed with zinc dust and acetic acid, the filtrate gives a blue coloration when starch paste and a drop of fuming nitric acid are added. This reaction is used as a test for iodoform, but is only trustworthy when the solution to be tested does not contain an iodide, hydriodic acid, or an easily decomposed organic substance containing iodine, and hence does not give a blue coloration when fuming nitric acid and starch paste are added without previous reduction. The test is also inapplicable when the solution contains appreciable quantities of albumin.

                                                    E. W. W.

Liquid Acetylene Di-iodide. By EDWARD H. KEISER (*Amer. Chem. J.*, 1899, 21, 261—265. Compare Sabanéeff, this Journal, 1876, i, 55 ; and Paternò and Peratoner, Abstr., 1890, 1219).—Acetylene has no action on iodine in the cold, but when dry acetylene is gently warmed with some solid iodine, the gas is slowly absorbed ; the reaction is best carried out at 140—160°, and the colour of the iodine usually disappears in the course of 24—36 hours. The product, when cold, consists of a mass of crystals of the ordinary solid di-iodide (m. p. 73°), and an amber-coloured liquid, the yield of the latter being apparently greater if the temperature of the bath is kept at 150—160° than if at 120—130°; when cooled, the liquid gives a further separation of the solid di-iodide, and if cooled at − 23° solidifies, but partially melts when the temperature is slowly raised. By this process of solidification and partial fusion, or by fractional solution in 50 per cent. alcohol in which the solid di-iodide is practically insoluble, the liquid can be separated into its two constituents, the solid and a liquid di-iodide.

Liquid acetylene di-iodide is colourless, but in diffused daylight slowly turns violet; it boils at 185°, solidifies at −21°, has a sp. gr. of 3·0625 at 20°, is readily volatile with steam, and is insoluble in water but readily soluble in alcohol and organic solvents. The

vapour can be heated to 230° without undergoing decomposition. When left in contact with hydriodic acid, it is slowly transformed into the solid modification, and when treated with zinc dust and alcohol it yields acetylene. The two di-iodides are supposed to be stereoisomerides, the solid being regarded as the *trans-* and the liquid as the *cis*-modification.   J. J. S.

Direct Nitration of Paraffins. Higher Primary Nitro-paraffins. By R. A. WORSTALL (*Amer. Chem. J.*, 1899, 21, 210—218 and 218—238. Compare Abstr., 1898, i, 346).—Nonane, decane, hendecane, and dodecane have been nitrated according to the method previously described, and, in addition to nitro-derivatives, acetic, oxalic, and succinic acids and carbonic anhydride were always formed. With nonane, nitric acid of sp. gr. 1·08 was employed, and a 70 per cent. yield of mono- and dinitro-derivatives was obtained. Acid of the same strength was employed for decane, hendecane, and dodecane ; the nitro-derivatives were separated from unaltered hydrocarbon by conversion into sodium derivatives, which were extracted by water, decomposed by carbonic anhydride, and the nitro-derivatives extracted with ether, the mononitro- being separated from the dinitro- compounds by distillation in steam.

Nitrohexane boils at 180—181°, has a sp. gr. of 0·9605 at 17°, and yields hexoic acid when heated with concentrated hydrochloric acid at 160°. It is only slowly soluble in aqueous potassium hydroxide, but readily in alcoholic potash. The best method for obtaining its sodium derivative, $C_6H_{12}Na \cdot NO_2$, is to add a solution of sodium ethoxide in a mixture of alcohol and light petroleum to a solution of the nitro-compound in light petroleum ; it is a colourless salt readily soluble in water or alcohol, but insoluble in ether or carbon bisulphide ; it blackens when heated, but is not explosive. Dinitrohexane reacts with bromine water, yielding a heavy, oily bromide ; when reduced, the dinitro-compound yields ammonia as one product.

Nitroheptane boils at 193—195°, and has a sp. gr. of 0·9476 at 17° ; its sodium, mercuric, lead, and silver salts have been prepared. When the sodium derivative is added to an excess of bromine water, a heavy, oily *bromide*, $C_7H_{14}BrNO_2$, is obtained.

Nitro-octane boils at 206—210°, and has a sp. gr. of 0·9346 at 20°. Dinitro-octane has a sp. gr. of 1·0638 at 23°.

Nitrononane, $C_9H_{19}NO_2$, is a pale yellow liquid with a pleasant odour; it boils at 215—218°, but undergoes considerable decomposition, and has a sp. gr. of 0·9227 at 17°. Dinitrononane has not been obtained in a pure state.

The sp. gr. of *nitrodecane* at 15° is 0·9105, that of *nitrohendecane* is 0·9001 ; the amount of nitrododecane obtained was too small to admit of purification.

The sodium derivatives, nitrolic acids, and bromo-derivatives of most of these nitro-compounds are described ; the amines and corresponding platinochlorides were also prepared.   J. J. S.

Determination of the Structure of Substances with Labile Atom-groupings. By ARTHUR HANTZSCH (*Ber.*, 1899, 32, 575—600). —The author describes as *pseudo-acids* those substances which do not

contain a hydrogen atom directly displaceable by metals, but which are capable of changing into a salt-forming isomeride. The following tests may be used to recognise the existence of pseudo-acids. (1) If an aqueous solution of a hydrogen compound neutralises a base *gradually*, it is a pseudo-acid. (2) If a neutral or feebly acid hydrogen compound gives salts which are neutral or feebly basic, that is, are not dissociated hydrolytically, it is a pseudo-acid, and the salts are derived from a more strongly acid isomeride. In a case of this sort, a neutral solution of the salt, when mixed with an equivalent quantity of an acid, still remains neutral. (3) If a colourless hydrogen compound yields coloured salts and a coloured ion in solution, it is a pseudo-acid. (4) An abnormally large positive temperature coefficient in the conductivity or the dissociation constant of a solution, is an indication of a pseudo-acid. (5) If a hydrogen compound does not form a salt by direct combination with dry ammonia in a non-dissociating solvent, but does so in presence of water, it is a pseudo-acid ; the formation of a salt, however, does not prove it to be a true acid. Similarly, if phenylcarbimide, phosphorus pentachloride, and acetic chloride do not interact with a substance except in dissociating solvents, it is probabaly non-hydroxylic pseudo-acid. (6) If a substance does not combine directly with water or alcohol, but yields a stable hydrate or alcoholate by indirect methods, it is a pseudo-acid.

Most of the examples quoted in the paper are referred to in the succeeding abstracts, but the following are new. Violuric acid and other oximidoketones, $-CO\cdot C(NOH)-$, are colourless, but yield coloured salts derived probably from the form $-C(OH):C(NO)-$; paranitrophenol behaves similarly ; in all these cases, there is a very great increment in the conductivity of a solution between $0°$ and $25°$, which is accompanied by a deepening in the colour of the solution. The antidiazohydrates, $R_1\cdot N:NOH$, which are electrolytes, and therefore true acids, interact with phosphorus pentachloride, acetic chloride, and ammonia, but the non-electrolytic nitrosamines, $R_2\cdot NH\cdot NO$, do not ; Thiele's 'nitrosourethane' belongs to the former class, and is formulated by the author as $COOEt\cdot N:N\cdot OH$, whilst 'parabromodiazobenzene' is formulated as $C_6H_4Br\cdot NH\cdot NO$. The potassium derivative of hydroxy-azobenzene, $C_6H_5\cdot N:N\cdot C_6H_4\cdot OK$, by interaction with hydrochloric acid in aqueous solution, yields a hydrate which cannot be prepared directly by the action of water on the parent substance ; the latter is therefore regarded as the isomeric quinone hydrazone, $C_6H_5\cdot NH\cdot N:C_6H_4:O$.

When the salt-forming modification of a substance is not known in a free state, but only in the salts, or as an ion in aqueous solution, the author describes the case as one of '*ionisation isomerism.*'

Pseudo-bases are substances which, by isomeric change, are capable of giving a true base of the ammonium hydroxide type from which the salts are derived. Thus phenylmethylacridinium chloride,

$CPh\underset{C_6H_4}{\overset{C_6H_4}{\diagup\diagdown}}NMeCl$, is converted by alkalis into phenylmethyl-

acridinium hydroxide, $CPh\underset{C_6H_4}{\overset{C_6H_4}{\diagup\diagdown}}NMe\cdot OH$, which is almost as power-

ful a base as potash, and is highly dissociated in solution, but rapidly changes into the isomeric phenylmethylacridol, $CPh(OH) <^{C_6H_4}_{C_6H_4}> NMe$, which is an indifferent alcoholic pseudo-base, insoluble in water, and readily soluble in organic solvents. A large number of other ammonium-bases are referred to in the paper as probably belonging to the same class. T. M. L.

NOTE.—It has been shown by Brereton Baker (Proc., 1893, **9**, 129, 165) that ammonia and hydrogen chloride do not combine except in presence of moisture; hydrogen chloride would therefore be classified as a 'pseudo-acid,' according to the rules given in this paper. The chemical tests under the fifth heading do not, therefore, appear to be altogether trustworthy. The majority of the tests are only applicable to those cases in which the conversion of the free acid into the neutral pseudo-acid is virtually complete. T. M. L.

Isonitro-compounds. By ARTHUR HANTZSCH and A. VEIT (*Ber.*, 1899, **32**, 607—627. Compare Abstr., 1896, i, 353 and 672).—Nitromethane is a normal nitro-compound; it has no acid reaction, yields solutions of very low conductivity, and gives no coloration with ferric chloride. The salts, which are derived from isonitromethane, show an alkaline reaction, and give a red coloration with ferric chloride. The existence of isonitromethane in a free state is shown by the following facts. (1) When a cold solution of the sodium salt is acidified with hydrochloric acid, it gives a transient red coloration with ferric chloride. (2) A mixture of equivalent quantities of nitromethane and baryta water shows a decrease of conductivity during 15 minutes at 0°, as the base is *gradually* neutralised by the pseudo-acid. (3) Similarly, when a solution of the barium salt is mixed with an equivalent quantity of hydrochloric acid, the conductivity falls, during about 15 minutes, to that of the barium chloride in the solution, as the isonitromethane first formed passes into normal nitromethane. (4) When the barium salt is titrated with an equivalent quantity of hydrochloric acid, using methyl-orange as an indicator, a red colour appears on each addition of acid, but disappears again as the acid isonitromethane is converted into neutral nitromethane; a permanent red is first obtained when one equivalent of acid has been added to the salt, and the solution then ceases to give a red colour with ferric chloride. An aqueous solution of barium isonitromethane gradually decomposes into nitrous acid, hydroxylamine, formaldehyde, or formoxime, formic acid, and hydrocyanic acid. On adding acid to a concentrated solution of sodium isonitromethane, an intense red colour appears at the moment of neutralisation, but disappears with an excess of acid; this indicates the formation of methylnitrolic acid, $NO_2 \cdot CH\!:\!NOH$.

Bromonitromethane does not give any coloration with ferric chloride, and is a non-electrolyte. The sodium salt gives an intense coloration with ferric chloride, which persists for some time when the solution is acidified; the bromisonitromethane, the presence of which is thus indicated, changes into the normal form at least as rapidly as isonitro-

methane, but soon decomposes into hydrogen bromide, nitrous acid, and other products.

Dibromonitromethane behaves similarly, but the salts are still more unstable.
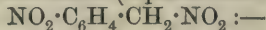
Nitroethane :—Sodium isonitroethane gives a deep blood red coloration with ferric chloride, which persists for half an hour in the acidified solution ; isonitroethane could not, however, be isolated. On passing hydrogen chloride into the sodium salt suspended in ether, a transient blue coloration appears, and ethylnitrolic acid is produced. The barium salt is alkaline, and behaves like barium isonitromethane when titrated with hydrochloric acid ; if the whole of the acid is added at once, about 5 per cent. of the isonitroethane is decomposed into hyponitrous acid and aldehyde ; this decomposition only takes place with excess of acid, thus explaining the contradictory statements of Nef (Abstr., 1895, i, 3) and V. Meyer (Abstr., 1895, i, 197). The neutralisation of nitroethane by caustic soda occupies about 40 minutes at 0°, but only 3 minutes at 25°, as indicated by the conductivity. The fall of conductivity on neutralising the barium salt with hydrochloric acid occupies about 2 days at 25°. Isonitroethane is about as strong an acid as acetic.

Nitropentane, contrary to the statement of V. Meyer (this Journal, 1872, 474), forms a sodium salt ; this has an alkaline reaction, and with ferric chloride gives a red coloration, which also appears in a freshly acidified solution.

Phenylnitromethane (ω-nitrotoluene) :—The ammonium salt, which melts at 89—90°, is precipitated by dry ammonia from a solution of the iso-, but not of the normal, nitro-compound ; phenylisonitromethane also interacts with phenylcarbimide and with phosphorus penta-chloride, but no definite product was isolated. On titrating the sodium salt with hydrochloric acid, the solution only becomes neutral very slowly, owing to the great stability of isophenylnitromethane ; about 5 per cent. of the substance is decomposed into benzaldehyde and nitrous oxide.

Bromophenylnitromethane (ωω-bromonitrotoluene), $CPhBr\cdot NO_2$, is indifferent to ferric chloride, but the sodium salt yields an intense black colour with ferric chloride ; the sodium salt decomposes in the solid state and very rapidly in solution, with formation of sodium bromide ; the free isonitro-compound is still more unstable.

Paranitrophenylnitromethane (ω-paradinitrotoluene),
$$NO_2\cdot C_6H_4\cdot CH_2\cdot NO_2 :—$$
The isonitro-compound described by Holleman (Abstr., 1897, i, 409) can be kept in a desiccator for a day before it loses its ferric chloride reaction, but it is much less stable in solution, the order of decreasing stability being given by the series,—chloroform, benzene, ether, alcohol, water. The isonitro-compound, unlike the normal form, interacts with phenylcarbimide and with phosphorus pentachloride. The sodium, ammonium, and copper salts each exist in two modifications. Paranitrophenylnitromethane is very sensitive to the action of excess of alkali, which decomposes it into sodium nitrite and a substance melting at 225°, which is probably a stilbene derivative.

Isonitracetophenone yields a neutral sodium salt, for which

$\lambda\infty = 74\cdot0$; from this, $\lambda\infty$ is calculated to be $24\cdot8$ for the anion, and 350 for the acid. The dissociation-constant of isonitracetophenone is $K = 0\cdot0063$, and it is therefore a stronger acid than benzoic. Since the acid modification is stable in solution, the conductivity immediately reaches a constant value on mixing equivalent quantities of the sodium salt and hydrochloric acid, or of the isonitro-compound and caustic soda.

Isonitracetone [see footnote, this vol., i, 433] yields a neutral sodium salt which does not colour a solution of potassium iodide and starch; isonitracetone itself decomposes rapidly even at $0°$, and although a very good electrolyte, it does not show a constant conductivity.

Potassium isodinitromethane is neutral and gives no coloration with ferric chloride; from the conductivity of an aqueous solution, the molecular conductivity of isodinitromethane was calculated to be $\lambda\infty = 237$ at $0°$. The dissociation constant, determined from a mixture of the potassium salt with hydrochloric acid, was $K = 0\cdot0143$, whilst a mixture of the silver salt with hydrochloric acid gave $K = 0\cdot0138$ at $0°$; at $25°$, $\lambda\infty = 369$ and $K = 0\cdot0268$; isodinitromethane is therefore about 8 times as strong as acetic acid. The large temperature coefficient for K shows that the aqueous solution contains normal as well as iso-dinitromethane; the colourless oil which is obtained by extracting with ether has an acid reaction and is probably also a mixture (compare nitracetone).

Bromodinitromethane.—A mixture of the potassium salt with hydrochloric acid was found to have a constant conductivity, showing that the isonitro-compound does not pass over into the normal form in aqueous solution; subtracting the value for potassium chloride, $\lambda = 20\cdot1$ for a concentration $N/64$; this substance is a stronger acid than dinitromethane.

Dinitroethane behaves quite differently from dinitromethane, and resembles rather mononitromethane. The conductivity of a mixture of the potassium salt with an equivalent quantity of hydrochloric acid falls after about a quarter of an hour at $0°$ to that of the potassium chloride in the solution, owing to the conversion of the isodinitroethane into the normal form. On titrating a solution of the potassium salt with an equivalent quantity of hydrochloric acid, results are obtained similar to those which have been described for barium isonitromethane; the isonitro-compound is, however, more labile, and the red coloration never lasts more than 30 seconds. The resulting solution still contains a trace of isodinitroethane (although this cannot be determined from the conductivity), since it is acid to litmus and is still slightly yellow; the yellow colour only disappears when an excess of acid has been added.

The authors point out that amongst the derivatives of nitromethane the stability of the isonitro-compound and its acid character increases with the negative character of the radicle, as is seen in the series isonitro-methane and -ethane, phenyl-isonitromethane, parabromo- and paranitro-phenylisonitromethane, benzoyl- and acetyl-isonitromethane (isonitracetophenone and isonitracetone). T. M. L.

Nitroform. By ARTHUR HANTZSCH and A. RINCKENBERGER (*Ber.*, 1899, **32**, 628—641).—By the action of alcoholic potash, tetranitromethane is converted into ethylic nitrate and *potassium nitroform*. This is a yellow salt, which explodes between 97° and 99°, and gradually decomposes at ordinary temperatures, leaving a residue of pure potassium nitrate, according to the equation $2C(NO_2)_3K = 2KNO_3 + 2CO_2 + 2NO + N_2$. The aqueous solution is yellow, the molecular conductivity is $\lambda_{32} = 51 \cdot 9$ at 0°, and at 25° $\lambda_{32} = 98 \cdot 3$, $\lambda_{1024} = 111 \cdot 2$, the difference $\lambda_{1024} - \lambda_{32}$ being exactly the same as for potassium chloride. The *sodium* salt gave $\lambda_{32} = 80 \cdot 2$, $\lambda_{64} = 83 \cdot 0$, whence $\lambda\infty = 94 \cdot 1$, and for the acid $\lambda\infty = 325 + 45 = 370$ at 25°. The *ammonium* salt explodes at 200°, and decomposes slowly at ordinary temperatures, leaving a residue of ammonium nitrate.

On adding an excess of sulphuric acid to a solution of potassium nitroform, the yellow colour disappears, and, by extracting with ether, normal nitroform can be obtained in colourless crystals melting at 15°. Anhydrous solutions of nitroform in benzene, light petroleum, chloroform, carbon bisulphide, and absolute ether are colourless, but the merest trace of water develops the yellow colour characteristic of isonitroform. Whilst isonitromethane is a very feeble acid, isodinitromethane is a fairly strong acid, and isonitroform is one of the strongest organic acids, the degree of dissociation being too high to determine the affinity constant; thus, at 25°, the degree of dissociation is 88·1 per cent. at $N/32$, and 94·9 per cent. at $N/512$, whilst at 0° it is 96·7 per cent. at $N/512$. The temperature coefficient of conductivity is comparable with that of hydrochloric acid. The strength of the acid is illustrated by the fact that the degree of dissociation is not altered by mixing with an equivalent quantity of hydrochloric acid; the solution has a mean conductivity, and it is only when there is a very large excess of the mineral acid that the yellow colour of the ion begins to disappear. Contrary to the statement of V. Meyer (this Journal, 1875, 1256), nitroform is quite a stable substance, and can be distilled with steam either alone or in presence of sulphuric acid; the vapour is colourless, and the substance, therefore, distils as true nitroform, but condenses to a yellow solution.

The *silver* salt, $C(NO_2)_3Ag + H_2O$, dissolves in water or ether, and is regarded by the author as having the formula $CH(NO_2)_2 \cdot NO(OH) \cdot OAg$, corresponding with that of the alcoholates described later; it is neutral, melts at 100°, decomposing at 106°, and slowly at ordinary temperatures. By interaction with methylic iodide, it yields trinitroethane $CMe(NO_2)_3$, identical with that described by Franchimont (Abstr., 1887, 466). In just the same manner as tetranitromethane is converted into trinitromethane and ethylic nitrate by the action of alcoholic potash, trinitromethane is converted by the action of aqueous potash into potassium dinitroethane and potassium nitrate; the product is identical with the potassium salt prepared by Chancel (Abstr., 1883, 914) and by ter Meer (Abstr., 1876, ii, 185) from the product of the action of nitric acid on ethylic methylacetoacetate. If alcoholic potash is used, the product is an *alcoholate*, to which the author ascribes the formula $CHMe(NO_2) \cdot NO(OK) \cdot OEt$; this

salt is very stable, it separates from alcohol in yellow leaflets and also crystallises unaltered from hot water in long, slender needles; it differs entirely from the potassium salt of dinitroethane, and gives a silver salt which also contains 1 mol. of alcohol. The corresponding acid, *dinitroethane alcoholate*, was obtained as a yellow oil with a faint smell and slight acid reaction; unlike dinitroethane, this acid, when prepared from the potassium salt and hydrochloric acid, does not pass into an indifferent pseudo-acid, but remains as a true acid for which $\lambda\infty = 356\cdot4$ and $K = 0\cdot0164$ at $25°$; it is thus ten times as strong as acetic acid. The alcohol was not removed from the potassium salt by boiling with water or by dissolving in sulphuric acid, and, conversely, the alcoholates could not be prepared by the action of alcohol on dinitroethane or its potassium salt; the series of compounds is similar to the compounds of sodium methoxide with trinitrobenzene (V. Meyer, Abstr., 1896, i, 419), and with picric ethers (Jackson and Ittner, Abstr., 1897, i, 332; and Jackson and Boos, Abstr., 1898, i, 517). T. M. L.

Cyanoform. By ARTHUR HANTZSCH and G. OSSWALD (*Ber.*, 1899, 32, 641—650. Compare Schmidtmann, Abstr., 1896, i, 458).—When cyanoform is shaken up with water and ether, three layers are produced (Schmidtmann) just as is the case with water, ether, and succinonitrile (Schreinemaker, Abstr., 1898, ii, 329); the composition of the middle layer is fairly constant, and may be represented roughly by the formula $CH(CN)_3 + 10H_2O + 10Et_2O$.

Pure cyanoform rapidly polymerises to a yellow, crystalline mass (Schmidtmann), as is readily seen on allowing an ethereal solution to evaporate, but the aqueous solution is remarkably stable, although it acquires a greenish-yellow colour by exposure to air; it can be titrated sharply with caustic soda and phenolphthalein, and is unaltered by boiling with dilute acids and alkalis; it is not appreciably volatile with steam. The aqueous solution appears to consist chiefly of *isocyanoform*, $C(CN)_2\text{:}C\text{:}NH$, and it is from this that the salts are derived.

Sodium isocyanoform has a molecular conductivity $\lambda\infty = 91\cdot4$, from which the molecular conductivity of the acid is calculated to be $\lambda\infty = 367$. Isocyanoform is an even stronger acid than isonitroform, the degree of dissociation being $92\cdot5$ per cent. at $N/32$, and $97\cdot6$ per cent. at $N/1024$ at $25°$. *Ammonium cyanoform*, $C(CN)_2\text{:}C\text{:}N\cdot NH_4$, is a well-crystallised neutral salt, and melts with decomposition at $183°$; with excess of ammonia, it gives a liquid product which has approximately the composition $CH(CN)_3,3NH_3$; this is analogous to the liquid product formed by ammonium nitrate (Divers, Abstr., 1873, 598; 1898, ii, 508).

The alcoholate described by Schmidtmann is regarded as dicyanacetimidoethylic ether, $CH(CN)_2\cdot C(OEt)\text{:}NH$; unlike cyanoform, its aqueous solution is neutral, but slowly becomes acid when boiled as the cyanoform is regenerated; it is insoluble in ammonia, but dissolves in cold caustic soda, from which it is at first precipitated unchanged by acids, but afterwards passes back into cyanoform.

When silver cyanoform is heated with methylic iodide, it is converted into *tricyanoethane*, $CMe(CN)_3$, which sublimes in fine, colourless needles

and melts at 93·5°; it is readily soluble in all organic solvents except light petroleum, but, unlike cyanoform, is soluble in water. When boiled with water, it is decomposed into cyanic acid, $(CO_2 + NH_3)$, and a substance melting at 60—65°, which is probably methylmalonodinitrile, $CHMe(CN)_2$; when boiled with soda, it is hydrolysed to ammonia and methylmalonic acid.

With benzylic iodide, silver cyanoform interacts in the cold, forming *tricyanoethylbenzene*, $CH_2Ph \cdot C(CN)_3$; this crystallises from chloroform in yellowish needles, melts at 138°, and sublimes when heated carefully. It is more stable to hot water than tricyanoethane, but readily loses 1 mol. of cyanic acid in alcoholic solution, and is converted into *benzylmalonodinitrile*, $CH_2Ph \cdot CH(CN)_2$, which is deposited in colourless plates melting at 78—79°; it is neutral, dissolves in alcohol and ether, but not in water; when boiled with caustic soda, it is decomposed into ammonia and benzylmalonic acid.   T. M. L.

Cyanuric Compounds. By OTTO DIELS (*Ber.*, 1899, **32**, 691—702). —The resemblance between cyanuric derivatives and purine compounds suggested the possibility of reducing cyanuric chloride to the corresponding hydrogen compound, $C_3N_3H_3$. Although this step has not been found practicable, chlorocyanurodiamine yields diamidocyanuric hydride under the influence of hydriodic acid; this treatment converts several chlorocyanuramines into the corresponding derivatives of cyanuric hydride.

The symmetrical structure of the cyanuric molecule, represented by

the formula $N \underset{\underset{\cdot}{C=N}}{\overset{\overset{\cdot}{C}-N}{<}} >C\cdot$, is established by replacing single halogen

atoms in cyanuric chloride by three different amido-groups; if this operation is carried out in the three orders possible, the final product is found to be the same in each case.

Diamidocyanuric hydride, $C_3N_3H(NH_2)_2$, obtained by agitating chlorocyanurodiamide with fuming hydriodic acid and phosphonium iodide, crystallises from boiling water in long, lustrous needles; it softens at 320°, and melts and decomposes at 325° (329° corr.). The *hydrochloride, nitrate*, and *sulphate* are crystalline, and salts are also formed with the chlorides of platinum, gold, and mercury. The *diacetyl* derivative is insoluble in cold water, and dissolves sparingly in boiling water or acetone.

Cyanuramidodichloride, $C_3N_3Cl_2 \cdot NH_2$, prepared by passing ammonia into an ice cold ethereal solution of cyanuric chloride, and evaporating in a vacuum the filtrate from the ammonium chloride, crystallises from water, and does not melt below 400°; it dissolves very readily in alcohol, ether, chloroform, and acetone, and is scarcely soluble in cold water. When treated with boiling water in a reflux apparatus during $1\frac{1}{2}$ hours, it is converted into melanurenic acid, $NH_2 \cdot C_3N_3(OH)_2$; it is also soluble in alkali sulphides, yielding dithiomelanurenic acid, $NH_2 \cdot C_3N_3(SH)_2$.

Amidocyanuric dihydride, $C_3N_3H_2 \cdot NH_2$, produced on agitating cyanuramidodichloride with hydriodic acid and phosphonium iodide, crystallises from hot water in long, silky needles; it softens and

becomes brown at 215°, and melts and decomposes at 225° (228° corr.). The *aurichloride* forms long, yellow needles.

Cyanuramidomethylamidochloride, $NH_2 \cdot C_3N_3Cl \cdot NHMe$, prepared from cyanuramidodichloride and methylamine, crystallises from acetone in small plates containing $\frac{1}{2}H_2O$.

Methylethylmelamine (*cyanuramidomethylamidoethylamide*),

$$NH_2 \cdot C_3N_3(NHMe) \cdot NHEt,$$
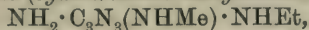
is obtained by heating the foregoing substance with aqueous ethylamine at 100—110° during 3—4 hours; it dissolves readily in hot water, separating slowly from the cold solutions in ill-defined crystals melting at 174° (176° corr.). The *hydrochloride*, *sulphate*, and *nitrate* crystallise in needles, the last-named melting at 166° (corr.); the *oxalate* melts at 230° (corr.), and crystalline salts are also formed with the chlorides of platinum, gold, and mercury.

Cyanuroethylamidodichloride, $C_3N_3Cl_2 \cdot NHEt$, prepared by carefully adding an ethereal solution of ethylamine to cyanuric chloride dissolved in ether at $-20°$, crystallises in silky needles, and melts at 107·5° (corr.).

Cyanuramidoethylamidochloride, $NH_2 \cdot C_3N_3Cl \cdot NHEt$, obtained by the action of aqueous ammonia on the foregoing substance, crystallises from hot glacial acetic acid in aggregates of lustrous needles; it sinters at 170°, and melts at 177° (corr.). When heated with aqueous methylamine at 120—125° during 3—4 hours, it yields methylethylmelamine.

Cyanuromethylamidodichloride, prepared from ethereal cyanuric chloride and methylamine at $-20°$, dissolves readily in ether, alcohol, acetone, and chloroform; it crystallises from water in long, silky needles, sinters at 156°, and melts at 163° (corr.).

Cyanuromethylamidoethylamidochloride, $NHMe \cdot C_3N_3Cl \cdot NHEt$, produced on treating the foregoing substance with aqueous ethylamine, crystallises from glacial acetic acid in stellar aggregates; it sinters at 225°, and melts at 238° (corr.). Aqueous ammonia at 110° converts it into methylethylmelamine.　　　　　　　　　　　　　　　M. O. F.

An Isomeride of Potassium Ferricyanide. By JAMES LOCKE and GASTON H. EDWARDS (*Amer. Chem. J.*, 1899, **21**, 193—206). According to Städeler (*Annalen*, 1869, **151**, 1), Bong (this Journal, 1876, i, 907) and Skraup (*ibid.*, 1877, ii, 598), potassium ferricyanide when oxidised, forms the compound $K_2FeC_6N_6$. The authors have attempted to prepare it by Skraup's method, but cooled down the liquid so that practically no evolution of gas (cyanogen chloride) occurred; the crystalline product thrown down on the addition of alcohol was purified by dissolving in water and reprecipitating with alcohol. The salt obtained after precipitating thrice with alcohol appeared to be homogeneous under the microscope, and consisted of very small, greenish-yellow needles; after exposure for several days in a vacuum over sulphuric acid, its composition corresponds with that required by the formula $K_3FeC_6N_6, H_2O$. This potassium β-ferricyanide, under suitable conditions, may be obtained in olive-coloured crystals of moderate size, and is not hygroscopic; it dissolves with the greatest readiness in water, the solution being comparatively stable,

although it undergoes gradual decomposition. When reduced with sodium amalgam in alkaline solution, it yields potassium ferrocyanide. Like the normal salt, potassium β-ferricyanide yields characteristic precipitates with solutions of salts of most of the heavy metals ; these in general have the same characteristics as the α-ferricyanides, and in some cases pass over into the latter with extreme ease. The bismuth, stannic, lead, and silver salts differ materially from the corresponding α-ferricyanides. Bismuth α-ferricyanide is a sparingly soluble, straw-coloured precipitate insoluble in concentrated nitric acid ; a solution of potassium β-ferricyanide, when freshly prepared, gives no trace of a precipitate with bismuth nitrate, but after some time, and especially on exposure to bright sunlight, large granules of a black, crystalline compound, probably bismuth ferrocyanide, are deposited. Stannic chloride forms a precipitate with the β-, but not with the α-isomeride. Lead β-ferricyanide is more readily soluble than the α-compound, Silver β-ferricyanide is obtained as a dark-brown, flocculent precipitate which can be readily filtered and washed ; when suspended in water and heated at 100°, it is transformed into the α-compound. β-Ferri-cyanic acid has not been isolated. J. J. S.

Action of Aluminium Amalgam on Alcohols. By WETSCHIAS-LAW E. TISTSCHENKO (*Chem. Centr.*, 1898, i, 91 ; from *J. russ. chem. Ges.*, **29**).—By the action of aluminium amalgam on alcohols, the corresponding aluminium alkoxides (*J. russ. chem. Ges.*, **28**, 412) are obtained. *Aluminium butoxide* boils at about 285° under 10—12 mm. pressure, the *iso-amyloxide* at 281° under 3·5—4 mm. pressure, and the *isopropoxide* at about 170° under 16 mm., and at about 150° under 4 mm. pressure. The *aluminium* derivatives of *secondary butylic alcohol* and of *methylpropylcarbinol* were also prepared. Trimethyl-carbinol and dimethylethylcarbinol are attacked by the amalgam, but the products were not obtained in a pure state ; tertiary amylic alcohol and isobutylic alcohol, however, yield substances which appear to crystallise in colourless needles (compare Hillyer, Abstr., 1897, i, 546). Aluminium amalgam acts on ethylic malonate and ethylic acetoacetate, giving, in the latter case, a compound whose properties are identical with those of Conrad's compound. The action of the amalgam on alcohols is not as violent as that of sodium amalgam ; the primary are more easily attacked than the secondary alcohols, with the ex-ception of dimethylethylcarbinol. The lower the molecular weight of the alcohol, the more readily the action takes place, the higher alcoholic groups being easily replaced by the lower, thus the isobutyl-oxide yields the methoxide or ethoxide by the action of methylic or ethylic alcohol, and the aluminium compounds of allylic alcohol, glycol, and ethylic acetoacetate may also be prepared in this way.
E. W. W.

Decomposition of Barium Isobutylic Sulphate. By EUG. BIRON (*Chem. Centr.*, 1898, i, 885 ; from *J. russ. chem. Ges.*, **29**, 697—698).—Barium isobutylic sulphate, prepared by Wurtz's method, begins to decompose at 130°. The gaseous products were absorbed in hydriodic acid and found to contain two-thirds isobutylene and one-third pseudobutylene. E. W. W.

Characteristic Derivatives of Geraniol and Citronellol. By JULIAN FLATAU and HENRI LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], **19**, 83—88. Compare Abstr., 1898, i, 618).—Geranyl phthalate (*loc. cit.*) yields a crystalline *silver* salt which melts at 132—133° and is very sparingly soluble in boiling water, whilst the *silver* salt prepared from citronellyl phthalate melts at 117—118°. When bromine is added to a solution of geraniol in acetic acid, it gives rise to *geraniol tetrabromide*, a yellow oil which has a sp. gr. 1·424, and cannot be caused to solidify; the corresponding *phthalate*, prepared by adding the calculated quantity of bromine dissolved in five times its weight of glacial acetic acid to a solution of geranyl phthalate in the same solvent, is a non-crystallisable oil which yields a *barium* salt, $(C_{18}H_{17}O_4Br_4)_2Ba + 4H_2O$. This is a white powder which is almost insoluble in water, and, when heated, softens at 90°, melts at 95°, and at 125° loses water and decomposes. The *aluminium* salt, $C_{54}H_{69}O_{17}Br_6Al$, prepared from the dibromide of citronellyl phthalate, is almost insoluble in water, and decomposes when heated.

The additive compounds, formed by the action of hydrogen bromide on geranyl and citronellyl phthalates, are being studied.

<div align="right">W. A. D.</div>

Chlorinated Derivatives of Trioxymethylene. By GIUSEPPE GRASSI-CRISTALDI and C. MASELLI (*Gazzetta*, 1898, **28**, ii, 477—500).—The interaction of acetic acid and paraformaldehyde gives a hydrated *trioxymethylene acetate*, $2CH_2(O \cdot CH_2 \cdot OH)_2, 11CH_3 \cdot COOH$, a white, gelatinous mass, gradually melting on heating and boiling at 103·5—104°; on treating it with a large quantity of water, the acetic acid is removed, yielding *trioxymethylene hydrate*, $CH_2(O \cdot CH_2 \cdot OH)_2$, melting at 107—109°. Cryoscopic determinations show that, in acetic acid solution, trioxymethylene hydrate suffers dissociation with the formation of dioxymethylene (diformaldehyde), which, however, has not been isolated. When dry hydrogen chloride is passed over para-formaldehyde at 130°, symmetrical dichloromethylic ether distils off as a colourless, oily liquid which boils at 104—106°, and undergoes decomposition in contact with moist air; its sp. gr. is 1·322 at 22°, Butlerow's value being 1·315 at 20°. If the paraformaldehyde is heated to 180° and the hydrogen chloride stream increased, methylene chlorhydrin is obtained, in addition to the dichlor-ether already mentioned; the chlorhydrin is a liquid boiling at 166°, and by the action of dehydrating agents is converted into symmetrical dichloromethylic ether. Trioxymethylene acetate absorbs dry hydrogen chloride, forming dichlorotrioxymethylene, or symmetrical dichloromethylal, which boils at 102—104°, and has sp. gr. 1·264 at 22°; cryoscopic measurements show that, in acetic acid solution, it has the normal molecular weight.

When heated with fused sodium acetate, dichlorotrioxymethylene gives the diacetyl derivative of dihydroxymethylic ether, $O(CH_2 \cdot OAc)_2$, which boils at 208—209°, is insoluble in water, but dissolves in alcohol, ether, acetic acid, and benzene, and in the last-named solvent gives the normal depression of freezing point. The corresponding tri-oxymethylene acetate, $CH_2(O \cdot CH_2 \cdot OAc)_2$, produced by the action of sodium acetate on methylene chlorhydrin, is a liquid boiling at

245—246°; it is soluble in water and in the ordinary organic solvents, and, dissolved in benzene, has the normal molecular weight.

In presence of aluminium chloride, dichlorotrioxymethylene and benzene condense, giving diphenylmethane, which is also obtained by the condensation of methylene chlorhydrin with benzene; these two, if dissolved in carbon bisulphide, and in presence of zinc chloride or zinc dust, give rise to benzylic chloride.   T. H. P.

Action of Potash on Epichlorhydrin in the Presence of Alcohols. By V. ZUNINO (*Real. Accad. Linc.*, 1897, ii, 348—350).—With the method commonly employed for the preparation of the ethers of glycerol, which consists in treating dichlorhydrin with sodium alkyloxides, the yield is small, owing to the occurrence of secondary reactions. Much better results are obtained by adding epichlorhydrin to the theoretical amount of the alcohol containing 10 per cent. of potassium hydroxide in solution, and in this way the following ethers were prepared, the figures indicating boiling points and specific gravities at 21°. Diethylic ether, 190—191°, 0·920 ; dimethylic ether, 169°, 0·915 ; dipropylic ether, 215—217°; diallylic ether, 225—227°, 0·991 ; di-isoamylic ether, 269—270°, 0·912.   N. L.

Lithiummethylammonium. By HENRI MOISSAN (*Compt. rend.*, 1899, 128, 26—30).—When methylamine, free from ammonia, is liquefied in contact with sodium, potassium, or calcium, no combination takes place, and no blue solution is formed, even after prolonged contact, but with lithium, a deep blue solution is formed at once with development of heat. After remaining for some time at the ordinary temperature, the very thick and very dark blue liquid has the composition $NH_2MeLi,2NH_2Me$, and is analogous to the compound formed by ammonia. When heated, or when placed in a vacuum, this liquid is decomposed and crystallised lithium is left, but no gas other than methylamine is liberated. If, however, the liquid is allowed to decompose until a small quantity of lithium is liberated, the compound NH_2MeLi, *lithiummethylammonium*, is obtained as a crystalline solid with a metallic lustre. It is stable at the ordinary temperature, but decomposes somewhat rapidly in a vacuum or when heated. When mixed with ether, it yields a blue solution stable at the ordinary temperature, but if an excess of ether is added, the blue colour disappears and a grey solid separates which is decomposed by water. Benzene and terebenthene decompose the lithiummethylammonium, and it reacts violently with carbon tetrachloride, chloroform, or ethylic iodide, combines with oxygen and nitrogen at the ordinary temperature, and is decomposed by cold water with liberation of hydrogen and methylamine, and formation of lithium hydroxide.   C. H. B.

Amines and Amides derived from Aldehydes. By MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1898, [vii], 15, 469—576).—This paper contains a discussion of the author's work on formaldehyde and hexa-methylenetetramine, together with experimental details previously recorded. (Compare Abstr., 1896, i, 78, 519, 586, 637 ; 1897, i, 394, 456, 457, 504, 505, 586 ; ii, 87, 131, 359 ; 1898, i, 120, 362, 462, and this vol., i, 186, 234, 246 ; ii, 142.)   G. T. M

Preparation of Hydroxyethylamines. By Felix Chancel (*Compt. rend.*, 1899, **128**, 313—314).—Contrary to Wurtz's statement (*Repert. chim.*, 1862, 42), a considerable quantity of trihydroxyethylamine hydrochloride is formed by acting on glycol chlorhydrin with warm, aqueous ammonia; the *aurichloride* of the base crystallises from water in monohydrated, golden leaflets and melts at 68°. The platinochlorides of both mono- and di-hydroxyethylamine crystallise with $1H_2O$, and are separated with difficulty; the normal *oxalate* of monohydroxyethylamine is a white substance which dissolves easily in water but sparingly in alcohol. W. A. D.

Synthesis of Propanediolamines by the Action of Ammonia and Amines on Glycide. By Ludwig Knorr and Eduard Knorr (*Ber.*, 1899, **32**, 750—757).—1-Aminopropane-2 : 3-diol- (γ-amidopropylenic αβ-glycol), $NH_2 \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, is made by allowing a mixture of glycide (1 part) and 25 per cent. ammonia solution (100 parts) to remain for some hours at ordinary temperatures, and is isolated by fractional distillation, which is finally conducted under reduced pressure; aminodipropanediol and aminotripropanediol are also produced in small quantities. It forms a pale yellow, very viscid liquid having a faint basic odour; its aqueous solution is alkaline to litmus, and may be accurately titrated with methylorange. It is excessively hygroscopic, and absorbs carbonic anhydride with avidity. It boils and decomposes slightly at 264—265° under 739 mm. and at 238—239° under 325 mm. pressure, and has the following physical constants :—Refractive power n_D 1·4900; sp. gr. 1·1752 at 20°/4°; molecular refraction $M_{Na} = 22·39$, the number calculated being 22·55. The substance has already been obtained by Chiari (this vol., i, 325) from acetyl dibromopropylamine, but the method is one of great practical difficulty. The *hydrochloride* is obtained as a viscid syrup, and the *aurichloride* as an orange-yellow, resinous precipitate; the *oxalate* crystallises from dilute alcohol in shining leaflets and melts at 69—74°; the *picrolonate*, $C_3H_9O_2N,C_{10}H_8N_4O_5$, crystallises in rounded aggregates of prisms and melts and decomposes at 219—220°. A dilute aqueous solution of aminopropanediol yields white precipitates with mercuric chloride and potassium cadmium iodide, a yellow precipitate with potassium bismuth iodide, and a caseous, white precipitate with tannin; with platinic chloride, picric acid, and potassium mercuric iodide, no precipitates are formed.

γ-*Methylamidopropylenic* αβ-*glycol*, $NHMe \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, is a colourless liquid which is viscid when cold but becomes mobile when hot, and boils at 235—250°. It is readily soluble in water and alcohol, sparingly soluble in ether, ethylic acetate, and acetone, and is insoluble in benzene. Its aqueous solution is strongly alkaline, and may be accurately titrated with methyl-oran.e as indicator. The free base rapidly absorbs carbonic anhydride and moisture. The *hydrochloride* is obtained as a viscid syrup. The *picrolonate*, $C_4H_{11}O_2N,C_{10}H_8N_4O_5$, crystallises from alcohol in orange prisms and melts, after sintering slightly, at 212°; an *isomeric picrolonate* is obtained at the same time, and its formation probably indicates that

the production of the base is accompanied by that of β-methylamido-propylenic $\alpha\beta$-glycol.

γ-*Dimethylamidopropylenic* $\alpha\beta$-*glycol*, $NMe_2 \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, obtained by the action of glycide on a solution of trimethylamine, is identical with the substance obtained by Roth (*Ber.*, 1882, **15**, 1173) by the action of trimethylamine on monochlorhydrin. It is a colourless, viscid, hygroscopic, basic oil which dissolves more readily in ether and chloroform than do the corresponding amido- and methylamido-glycols. The *methiodide*, $C_6H_{16}NO_2I$, crystallises from absolute alcohol in characteristic shining, orange leaflets, and melts at 133—134° ; the picrolonate separates from absolute alcohol in bright yellow, spherical aggregates, and melts without decomposing at 160°.

γ-Ethylamidopropylenic $\alpha\beta$-glycol, $NHEt \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, distils at 145° under a pressure of 25 mm. [Chiari (*loc. cit.*) gives 141—142° under a pressure of 18 mm.], the *picrolonate* separates from absolute alcohol as a bright yellow, crystalline mass and decomposes at 237°.

γ-Diethylamidopropylenic $\alpha\beta$-glycol, $NEt_2 \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, boils at 233—235° under 748 mm. pressure [Roth (*loc. cit.*) gives 233—235°]. The *picrolonate* crystallises from absolute alcohol in concentrically grouped, shining needles having a deep orange-yellow colour ; it melts without decomposing at 116—118°. A. L.

Diazoamido-compounds of the Fatty Series. By JOHANNES THIELE and WILHELM OSBORNE (*Annalen*, 1899, **305**, 64—80).—*Diazo-guanidine cyanide* (*triazendicarbamidine nitrile* or *amidoimidomethyl-cyanotriazen*), $NH\!:\!C(NH_2) \cdot NH \cdot N\!:\!N \cdot CN$, precipitated on mixing aqueous solutions of diazoguanidine nitrate and potassium cyanide, crystallises from water in small, yellow needles, which become brown above 200°, and melt indefinitely at higher temperatures, undergoing complete decomposition ; the nitrate melts at 123°.

Triazendicarbamidine amide, $NH\!:\!C(NH_2) \cdot NH \cdot N\!:\!N \cdot CONH_2$, crystallises from hot water in yellow needles containing $1H_2O$, and detonates at 139° without fusing ; the *hydrochloride* is obtained on heating diazoguanidine cyanide with hydrochloric acid at 60—70°. The *nitrate* crystallises in lustrous needles, and explodes at 136° ; the *silver nitrate* compound, $C_2H_6N_6O + AgNO_3$, is exceedingly hygroscopic. Boiling water resolves the hydrochloride into guanidine, nitrogen, carbonic anhydride, and ammonia.

Triazendicarbamidine amidoxime,
$$NH\!:\!C(NH_2) \cdot NH \cdot N\!:\!N \cdot C(NH_2)\!:\!NOH,$$
prepared from diazoguanidine cyanide and hydroxylamine, melts and decomposes at 144° ; ferrous sulphate develops a reddish-brown coloration in alkaline solutions, and boiling water resolves it into amido-tetrazole. The *nitrate* melts and explodes at about 80°, and the *hydrochloride* melts at 163° ; the sulphate dissolves with difficulty in cold water, and melts at 179°.
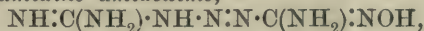
Triazendicarbamidine imido-ether is obtained in the form of *dihydro-chloride*, $NH\!:\!C(NH_2) \cdot NH \cdot N\!:\!N \cdot C(OEt)\!:\!NH,2HCl$, by the action of hydrogen chloride on diazoguanidine cyanide in presence of ether and absolute alcohol ; the salt melts at 107—110°.

The *ethylic* salt of triazendicarbamidine (*ethylic* amidoimidomethyltriazencarboxylate), $NH:C(NH_2)\cdot NH\cdot N:N\cdot COOEt$, prepared from the dihydrochloride of the imido-ether by the action of sodium carbonate, crystallises from water, and melts at $162°$; the *hydrochloride* yields crystals containing $1H_2O$, and melts at $155°$.

Triazendicarbodiamidine (*bisamidoimidomethyltriazen*),

$$NH:C(NH_2)\cdot NH\cdot N:N\cdot C(NH_2):NH,$$
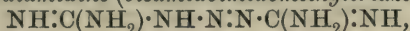
is obtained in the form of carbonate when the hydrochloride of the imido-ether is treated with alcoholic ammonia, and afterwards with sodium carbonate; it contains $1\frac{1}{2}H_2O$, becomes dark yellow at $150°$, and melts at $165°$. M. O. F.

Derivatives of Triazan (Prozan). By JOHANNES THIELE and WILHELM OSBORNE (*Annalen*, 1899, **305**, 80—96. Compare Abstr., 1898, i, 120).—Ethylic amidoimidosulphomethyltriazancarboxylate, $NH:C(NH_2)\cdot NH\cdot N(SO_3H)\cdot NH\cdot COOEt$, prepared by the action of sodium hydrogen sulphite on the amido-ether of triazendicarbamidine (foregoing abstract), crystallises from boiling water in slender, white needles, and melts at $180°$. Boiling aqueous alkalis eliminate one-half the available nitrogen from the substance, whilst boiling with acids resolves it into nitrogen, carbonic oxide, ethylene, sulphuric acid, ammonia, carbonic anhydride, hydrazine, and guanidine. The *amide*, $NH:C(NH_2)\cdot NH\cdot N(SO_3H)\cdot NH\cdot CONH_2$, obtained by triturating the amide of triazendicarbamidine with sodium hydrogen sulphite, crystallises from water in small, white needles, and melts at $141°$. Boiling caustic soda eliminates one-half of the nitrogen, sulphurous acid being also produced; boiling dilute sulphuric acid gives rise to sulphurous and formic acids, along with amidoguanidine. The *hydrochloride* crystallises with $1H_2O$, and melts at $105°$.

When diazoguanidine cyanide is reduced at the ordinary temperature, with zinc dust and acetic acid, amidoguanidine is produced; the ethylic salt of triazendicarbamidine yields guanidine and ethylic hydrazinecarboxylate. At the ordinary temperature, the amide of triazendicarbamidine gives rise to guanidine and semicarbazone; at $0°$, there is formed an unstable compound probably having the constitution $NH:C(NH_2)\cdot NH\cdot NH\cdot NH\cdot CONH_2$, but which undergoes decomposition even at low temperatures. M. O. F.

Acetyl Derivatives of Hydrazine. By ROBERT STOLLÉ (*Ber.*, 1899 **32**, 796).—Di-, tri-, or tetr-acetylhydrazine can be prepared by heating hydrazine hydrate with 3, 4, or 5 mols. of acetic anhydride respectively.

Diacetylhydrazine, $NHAc\cdot NHAc$, crystallises from hot alcohol in crusts, melts at $138°$, and boils at $209°$ under 15 mm. pressure, and is readily soluble in water, sparingly so in chloroform, and almost insoluble in ether, benzene, and light petroleum.

Triacetylhydrazine, $NAc_2\cdot NHAc$, is a colourless syrup; it boils at $180—183°$ under 15 mm. pressure, and is soluble in alcohol and ether, but seems to decompose on solution in water.

Tetracetylhydrazine, $NAc_2\cdot NAc_2$, separates from its solution in alcohol and ether in large crystals, or from ether in needles; it melts at

85°, boils at 141° under 15 mm. pressure, and decomposes at 300—350° under ordinary pressure into acetic anhydride and dimethylfurodiazole.

J. F. T.

Electrolytic Preparation of Dithionbisulphides. By CARL SCHALL and S. KRASZLER (*Zeit. Elektrochem.*, 1898, **5**, 225—226. Compare Schall, Abstr., 1897, i, 317).—The electrolysis of aqueous solutions of potassium methyl-, isobutyl-, or isoamyl-xanthates yields the corresponding bisulphides at the anode. When an aqueous solution of diethylammonium diethyldithiocarbamate is electrolysed, a deposit of tetrethylthiuram bisulphide, $S_2(CS \cdot NEt_2)_2$, is formed on the anode, whence it is washed by ether. The anodic deposit obtained from potassium phenylthiocarbazide, $NHPh \cdot NH \cdot CS \cdot SK$, consists of diphenylthiocarbazide, $CS(NH \cdot NHPh)_2$. An aqueous solution of potassium ethyltrithiocarbonate, $SEt \cdot CS \cdot SK$, yields the hitherto unknown dithionbisulphide, $S_2(CSEt)_2$, in the form of a yellow, uncrystallisable oil which readily decomposes. With aniline, it yields thiocarbanilide, sulphur, mercaptan, and hydrogen sulphide; phenylthiocarbimide was also found, probably owing to the intermediate formation of phenyldithiourethane.

T. E.

Compounds of Aldehydes with Mercuric Sulphate. By GEORGES DENIGÈS (*Compt. rend.*, 1899, **128**, 429—431).—Acetaldehyde yields the compound $SO_4:(HgO)_2:Hg,C_2H_4O$, which always contains a little mercurous sulphate, but formaldehyde does not form a similar compound, and simply reduces the mercuric salt to mercurous sulphate, the latter separating in a well crystallised form. This behaviour of the lowest homologue is analogous to that of ethylene and benzene, which likewise do not form compounds with mercuric sulphate. (Compare Abstr., 1898, i, 546, 618, and this vol., i, 22, and ii, 256.)

C. H. B.

Chloral-ammonia. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1898, [iii], **19**, 171—173. Compare Abstr., 1898, i, 462).—The molecular weight of this compound, determined by the cryoscopic method in glacial acetic acid, indicates a non-associated molecule; in benzene and ethylenic dibromide, it corresponds with the doubled formula.

G. T. M.

Methyloctenonal. By GEORGES LÉSER (*Compt. rend.*, 1899, **128**, 371—373).—The methyloctenonal previously described (this vol., i, 330) is very stable, boils without decomposing at 108—110° under 10 mm. pressure, and solidifies on cooling; under ordinary pressure, it boils at 205—210° and decomposes slightly. With hydroxylamine, it yields an isoxazole which boils at 113—114° under 16 mm. pressure, and reacts very energetically with sodium ethoxide, yielding a nitrile, $CMe_2:CH \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CN$, of the same percentage composition, which boils at 123—124° under a pressure of 16 mm., and when heated with alcoholic potash is converted into methylhexenamide (nacreous crystals melting at 85—86°), or by prolonged action into methylhexenoic acid, boiling at 216—218°. The ethyl derivative of the nitrile $CMe_2:CH \cdot CH_2 \cdot CH_2 \cdot CO \cdot CHEt \cdot CN$, when

heated with alcoholic potash, yields ammonia, formic acid, and methyl-nonenone boiling at 203—205° (compare this vol., i, 190).

Methyloctenonal forms an anilide which boils at 210—212° under 20 mm. pressure, and yields a crystallisable base when treated with concentrated sulphuric acid. With methylaniline, however, it forms a compound, $C_{16}H_{21}NO$, which boils at 214—216° under 17 mm. pressure, and this reaction, as well as others, can only be explained by assuming that methyloctenononal is tautomeric, and sometimes behaves as if it has the constitution $CMe_2:CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH:CH\cdot OH$, although generally its behaviour corresponds with the constitution $CMe_2:CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot CHO$. C. H. B.

A Reaction of Aldehydes and Ketones. By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. Chim.*, 1898, [iii], **19**, 134—137. Compare Abstr., 1897, ii, 470).—The use of aldehydes and ketones for increasing the reducing power of organic developers has already been studied by the authors, and the reaction is now proposed as a delicate test for compounds of the aldehydic or ketonic type. To apply the test, 25 c.c. of an aqueous (or alcoholic) solution of the substance under examination is mixed with 50 c.c. of an aqueous solution of sodium sulphite (7 per cent.) and pyrogallol (1·5 per cent.), or of sodium sulphite (20 per cent.), and quinol (2 per cent.), and the action of the liquid on a photographic plate is compared with that of 50 c.c. of the same test-solution to which 25 c.c. of water (or alcohol) has been added. In this way, it is possible to detect the presence of 1 in 25,000 of formaldehyde, 1 in 15,000 of acetaldehyde, and 1 in 2500 of acetone. The reaction is not, however, of universal application, since it is not given by paraldehyde, chloral, diketones, ketonic acids, ketonic alcohols, aromatic ketones, or by aromatic aldehydes other than those of simple function or those in which the other functions are of a neutral character. N. L.

Action of Ammonia on Dithioacetylacetone. By VICTOR VAILLANT (*Bull. Soc. Chim.*, 1898, [iii], **19**, 246—249).—On passing gaseous ammonia into, or mixing alcoholic ammonia with, an ethereal solution of dithioacetylacetone, the *additive* compound, $C_{10}H_{14}S_2O_4,2NH_3$, separates as a light-yellow, crystalline powder, which decomposes in the air, or on adding dilute acids, to form dithioacetylacetone; when the additive compound is left in a closed vessel, or is gently warmed on the water-bath, it loses water and yields yellow crystals having the composition $C_{10}H_{16}N_2S_2O_2$, which darken, when heated, at 120° and melt and decompose at 160°. The compound so obtained does not yield a metallic derivative when treated with copper acetate (compare Abstr., 1895, i, 168), and therefore probably has the constitution $S_2(CAc:CMe\cdot NH_2)_2$ rather than $S_2(CHAc\cdot CMe:NH)_2$; this view is in accord with the fact that the similar derivative of acetylacetone has the constitution $NH_2\cdot CMe:CHAc$, although that obtained from methylacetone appears to have the structure $CH_3\cdot CHAc\cdot CMe:NH$ (A. and C. Combes, Abstr., 1893, i, 454).

On adding alcoholic methylamine to an ethereal solution of dithio-

acetylacetone, a light yellow, crystalline *additive* compound separates, which decomposes in the air, dithioacetylacetone being regenerated.

<div align="right">W. A. D.</div>

Decomposition of Ferric Acetate. By W. HERZ (*Zeit. anorg. Chem.*, 1899, **20**, 16—20).—A pure neutral solution of ferric acetate can be evaporated to dryness on the water-bath without decomposition. If the solution is heated in a water-bath for 10 hours, a decomposition takes place and basic acetate and ferric hydroxide are formed. At the ordinary temperature, the solution is stable for weeks, but if impurities are present a yellow precipitate is quickly formed. At 44°, a reversible reaction takes place, as expressed in the equation $Fe(C_2H_3O_2)_3 + 2H_2O \rightleftharpoons Fe(OH)_2 \cdot C_2H_3O_2 + 2C_2H_4O_2$, and the liberated acetic acid has a catalytic action, which at first accelerates the decomposition.

<div align="right">E. C. R.</div>

Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on Ethylic Sodiomalonate. By LOUIS BOUVEAULT (*Bull. Soc. Chim.* 1898, [iii], **19**, 78—80).—On gradually adding ethylic chloroglyoxylate (1 mol.) to ethylic sodiomalonate suspended in ether, and subsequently distilling under a pressure of 10 mm., two fractions are obtained boiling at 140° and 220° respectively; the second of these is the larger, and consists of *ethylic carboxyoxalacetate*, $CH(COOEt)_2 \cdot CO \cdot COOEt$, whilst the first consists of triethylic methanetricarboxylate, formed, together with carbonic oxide, by the decomposition of the product of higher boiling point.

When phenylhydrazine (1 mol.) is added to ethylic carboxy-oxalacetate, it gives rise, not to the expected pyrazole derivative, $\overset{\displaystyle C(COOEt){=\!=}N}{\underset{\displaystyle CH(COOEt)\cdot CO}{\Big|}}{>}NPh$, but to ethylic malonate, together with the phenylhydrazide, $COOEt \cdot CO \cdot N_2H_2Ph$, of monethylic oxalate, melting at 113° (Bülow, Abstr., 1887, 138); it thus appears that, in this case, an acid is formed by hydrolysis, phenylhydrazine initially acting in the same manner as alkalis. This behaviour is similar to that which occurs in the case of ethylic brom- and dibrom-oxalacetates, which are decomposed by phenylhydrazine, although ethylic oxalacetate yields a normal derivative; the influence of the COOEt-group in diminishing stability is thus similar to that of a halogen. Ethylic carboxyoxalacetate is slowly decomposed by moisture, giving rise to oxalic acid.

<div align="right">W. A. D.</div>

Ethylic Methylenemalonate. B y GUSTAV KOMPPA (*Chem. Centr.*, 1898, ii, 1169; from *Oefversigt af Finska Vet.-Soc. Förhandlingar*, **40**). —From the products of the action of diethylamine and formaldehyde on ethylic malonate, the author has isolated, not only ethylic methylenedimalonate, $CH_2[CH(COOEt)_2]_2$, but also a polymeride identical with the compound which Zelinsky (Abstr., 1890, 364) obtained by the action of sodium ethoxide on methylenic iodide and ethylic malonate. It is best prepared by allowing a mixture of ethylic malonate (1 mol.) with formaldehyde (1 mol.) and diethylamine to remain at the ordinary temperature for several days, then separating

the oil and distilling in a vacuum. The fraction which boils at 140—200° under 25 mm. pressure forms an amorphous mass of the polymeride, which is easily soluble in hot alcohol, chloroform, and benzene. By distilling the oil under the ordinary pressure, ethylic methylenemalonate is obtained, which only changes to the polymeride after some time. *Ethylic dibromomethylenemalonate*, $CH_2Br \cdot CBr(COOEt)_2$, prepared by adding bromine to ethylic methylenemalonate, boils at 130—140° under 5 mm. pressure, with liberation of some hydrogen bromide. E. W. W.

A New Additive Action of Alkylenic Oxides. By WILHELM TRAUBE and E. LEHMANN (*Ber.*, 1899, **32**, 720—721).—When ethylic sodiomalonate, suspended in absolute alcohol, is treated with ethylenic oxide, it yields the sodium derivative of a colourless oil which, under the influence of alcoholic ammonia, is converted into the *amide*, $C_5H_{10}N_2O_3$, of hydroxyethylmalonic acid ; the substance crystallises in colourless needles, and melts at 150°. Ethylenic oxide also acts on ethylic sodioacetoacetate.

Chlorohydroxypropylmalonamide, $C_6H_{11}ClN_2O_3$, obtained by treating with alcoholic ammonia the product of the action of epichlorhydrin on ethylic sodiomalonate, separates from absolute alcohol in colourless crystals, and melts at 117—118°. M. O. F.

Transformation of Unsaturated Acids. Hexylaticonic Acid. By RUDOLPH FITTIG and EMIL STUBER (*Annalen*, 1899, **305**, 1—18).— Hexylaticonic acid is obtained by the action of a boiling 20 per cent. solution of caustic soda on hexylitaconic acid (compare Fittig and Hoeffken, this vol., i, 339) ; it crystallises in transparent nodules and in minute needles from ether and benzene respectively, and melts at 78—78·5° (compare Fittig, Abstr., 1893, i, 692). The *barium* and *calcium* salts contain $\frac{1}{2}H_2O$, and the *silver* salt, which is amorphous, rapidly becomes violet-brown when exposed to light. *Bromohexylisoparaconic acid*, $C_{11}H_{17}BrO_4$, obtained by treating hexylaticonic acid with a solution of bromine in chloroform, crystallises from carbon bisulphide in lustrous, transparent needles, which melt and decompose at 134—135° ; it is insoluble in cold water, but dissolves in water at 70—80°, from which it crystallises in thin, white needles melting at 145—146°.

Hexylisoparaconic acid, $C_{11}H_{18}O_4$, prepared by reducing bromohexylisoparaconic acid in dilute sulphuric acid with 4 per cent. sodium amalgam, crystallises from benzene in lustrous leaflets, and melts at 83—84° ; the *calcium* and *silver* salts are anhydrous.

Hexylisaconic acid, $C_{11}H_{16}O_4$, obtained from bromohexylisoparaconic acid by the action of caustic soda, crystallises from a mixture of ether and petroleum in lustrous plates, and melts at 57·5—58·5° ; reduction with sodium amalgam converts it into hexylisoparaconic acid. The *calcium* salt crystallises in long, slender needles containing $3H_2O$; the *silver* salt is amorphous, and slowly becomes violet under the influence of light. The *acid*, $C_{11}H_{18}O_5$, is also produced when bromohexylisoparaconic acid is treated with caustic soda, being separated from hexylisaconic acid by the comparatively sparing solubility of the calcium salt ; the authors regard it as ketoheptylsuccinic acid, but this point

remains undecided. It crystallises from the aqueous solution in nodules, and melts at 99—99·5°; the *barium* salt contains $1H_2O$, and the *calcium* salt is anhydrous. The *acid*, $C_{11}H_{18}O_4$, obtained by reducing the foregoing acid with sodium amalgam, crystallises in leaflets, and melts at 72—72·5°.

Undecodilactone, $C_{11}H_{16}O_4$, produced on heating bromohexylisoparaconic acid with water in a reflux apparatus, crystallises from a mixture of ether and petroleum in white nodules and melts at 66—67°; hexylisaconic acid is formed at the same time, and in much greater amount.

The *dibromide* of hexylitaconic acid, $C_{11}H_{18}Br_2O_4$, prepared by the action of bromine in chloroform on hexylitaconic acid, crystallises from a mixture of ether and petroleum and melts at 134—135°.
                                                          M. O. F.

Oxidation of Unsaturated Dibasic Acids. By RUDOLPH FITTIG and WILHELM KÖHL (*Annalen*, 1899, **305**, 41—52).—When itaconic acid is oxidised with an alkaline solution of potassium permanganate, itatartaric and hydroxyparaconic acids are produced. *Hydroxyparaconic acid*, $COOH \cdot C(OH){<}{CH_2 \cdot CO \atop CH_2 \cdot O}$, crystallises from carbon tetrachloride and melts at 104°. The *calcium* salt, which contains $2H_2O$, has been described by Morawski; the *barium* and *silver* salts are anhydrous.

Oxidation of citraconic and mesaconic acids gives rise to oxalic and pyruvic acids; phenylitaconic and phenylaticonic acids yield benzaldehyde along with malonic and oxalic acids.   M. O. F.

Oxidation of Isobutylitaconic, Isobutylcitraconic, and Isobutylmesaconic Acids. By RUDOLPH FITTIG and FRIEDRICH KAEHLBRANDT (*Annalen*, 1899, **305**, 52—63).—When isobutylitaconic acid is oxidised with an alkaline solution of potassium permanganate, it yields valeraldehyde along with malonic and oxalic acids; isobutylcitraconic and isobutylmesaconic acids give rise to oxalic, isocaproic, and isobutylpyruvic acids.

Isobutylpyruvic acid, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot COOH$, forms a crystalline mass which melts at 22°; it deliquesces when exposed to moist air, and is readily volatile in steam. The *calcium* salt contains $2H_2O$, and the *barium* salt $1H_2O$; the *silver* salt crystallises from warm water, and is sensitive to light. The *phenylhydrazone* crystallises from a mixture of ether and petroleum in aggregates of needles, and melts at 105°.   M. O. F.

Optically Active α-Methylmalic Acid (2-Methyl-2-butanoldioic Acid). By WILHELM MARCKWALD and S. AXELROD (*Ber.*, 1899, **32**, 712—716. Compare Schütz and Marckwald, Abstr., 1896, i, 203).—The authors have obtained optically active α-methylmalic (citramalic) acid from the racemic substance by the agency of brucine. The interest of this observation lies in the fact that the optically active compounds hitherto described have invariably contained one atom of hydrogen directly united with the asymmetric carbon atom.

d-*Citramalic acid* melts at 95°, and is extremely hygroscopic,

whereas the racemic compound melts at 119°, and is not hygroscopic; a 74 per cent. solution has the specific rotatory power $[a]_D$ 34·67°. The *brucine* salt dissolves readily in hot water, but is only sparingly soluble in cold.

The specific rotations of citramalic acid and the sodium salt have been recorded for various concentrations and wave-lengths.

M. O. F.

Synthesis of Terebic Acid. By EDMOND E. BLAISE (*Bull. Soc. Chim.*, 1898, [iii], **19**, 275—277).—Attempts to prepare terebic acid by the synthetical method suggested by Reformatsky, which consists in the condensation of acetone with ethylic bromosuccinate in the presence of metallic zinc, decomposition of the zinc compound thus produced with water, and hydrolysis of the ethylic diaterebate obtained, were unsuccessful, but on substituting a zinc–copper couple for the zinc, a product was readily obtained which was identified as terebic acid by analysis and by its conversion, on distillation, into 2-methyl-pentanolide. The yield is small (10 to 15 grams for every 100 grams of ethylic bromosuccinate employed) but much better than that obtained in the preparation of the acid by the oxidation of pinene. N. L.

Hydroxytrimethylsuccinic Acid and its Derivatives. By GUSTAV KOMPPA (*Chem. Centr.*, 1898, ii, 1168—1169; from *Acta. Soc. Scient. Fennicæ*, **24**, 1—14). A good yield of hydroxytrimethyl-succinic acid, $COOH \cdot CMe_2 \cdot CMe(OH) \cdot COOH$, is obtained by adding hydrochloric acid in small portions to a cooled mixture of powdered potassium cyanide with ethylic dimethylacetoacetate dissolved in ether. After remaining in a closed vessel for a week, the ethereal layer is poured off and mixed with twice its volume of concentrated hydrochloric acid; the mixture, after remaining 24 hours at the ordinary temperature, is heated on the water bath for a day and then evaporated. Hydroxytrimethylsuccinic acid separates from water or ethylic acetate in clear, rhombic crystals and melts at 155—159°, the exact temperature depending on the rapidity of heating; if the acid is kept, its melting point gradually sinks. The properties of the acid render somewhat doubtful its identity with Tiemann's hydroxy-trimethylsuccinic acid, obtained by the oxidation of pinene and with Kachler's acid prepared by the oxidation of camphor. It dissolves easily in water, alcohol, and hot ethylic acetate, is rather soluble in ether, slightly so in benzene and light petroleum, and is precipitated by copper sulphate, ferric chloride, and lead nitrate. The ammonium salt crystallises in flat needles and is very easily soluble in water; the silver salt, $C_7H_{10}O_5Ag_2$, is a white, amorphous substance insoluble in water; the calcium salt, $C_7H_{10}O_5Ca, + \frac{1}{2}H_2O$, does not dissolve in water unless allowed to remain with it for a long time, when a solution is obtained which, on evaporation, yields a brittle, glassy mass. *Hydroxy-trimethylsuccinanil*, $\begin{matrix} CMe_2\text{———}CO \\ | \\ CMe(OH) \cdot CO \end{matrix} > NPh$, prepared by boiling the acid with aniline, crystallises from dilute alcohol in small needles, melts at 145°, is easily soluble in most solvents, and slightly soluble in water and light petroleum. The corresponding *paratolil*, $C_{14}H_{17}O_4N$, crystallises from alcohol in needles, melts at 185°, and with acetic chloride

yields an *acetyl* derivative, $C_{16}H_{19}O_4N$, which crystallises from hot alcohol in flat needles, melts at 131°, and is slightly soluble in cold alcohol. *Acetylhydroxytrimethylsuccinic anhydride*, $C_9H_{12}O_5$, obtained by the prolonged action of acetic chloride on hydroxytrimethylsuccinic acid, crystallises from light petroleum in needles and melts at 68°; in this reaction, a compound of unknown composition is also formed, this melts at 142° and is insoluble in light petroleum. By the action of alcohol and hydrochloric acid, only a portion of hydroxytrimethylsuccinic acid is converted into the ethylic salt, which is better prepared by the action of ethylic iodide on the silver salt; it is a liquid which boils at 122—123° under 9 mm. pressure and has a sp. gr. of 1·066 at 18°. *Ethylic chlorotrimethylsuccinate*, $COOEt \cdot CMe_2 \cdot CMeCl \cdot COOEt$, prepared by heating at 83° a mixture of phosphorus pentachloride with hydroxytrimethylsuccinic acid dissolved in chloroform, boils at 114·5—115·5° under 12 mm. pressure, and when hydrolysed with hydrochloric acid, yields an acid which does not contain chlorine and is probably a β-lactone-carboxylic acid. By the action of phosphorus pentabromide on hydroxytrimethylsuccinic acid, a complex mixture is obtained, the presence of the alkylic groups apparently rendering the hydroxyl group more difficult to replace. E. W. W.

Condensations with Ethylic β-Chlorisovalerate. By CLEMENTE MONTEMARTINI (*Gazzetta*, 1898, **28**, ii, 305—312).—The author has succeeded in verifying the constitution assigned by him to the acid obtained by the action of chlorine on isovaleric acid (Abstr., 1898, i, 236). On heating the ethylic salt of the chlorinated acid in a closed tube with alcohol and potassium cyanide, cyanogen is substituted for the chlorine atom, and on hydrolysing the product by means of hydrochloric acid, asymmetrical dimethylsuccinic acid is obtained. The chlorine atom in the chlorisovaleric acid must therefore be in the β-position.

Ethylic malonate and ethylic β-chlorisovalerate when heated together with sodium ethoxide, give a condensation product which on hydrolysis with alcoholic potash yields for the most part ββ-dimethylglutaric acid, and probably is a derivative of the tribasic acid, $COOEt \cdot CH_2 \cdot CMe_2 \cdot CH(COOEt)_2$. T. H. P.

Formation of Carbamides. By AD. JOUVE (*Compt. rend.*, 1899, **128**, 114—115).—When a solution of carbonic oxide in ammoniacal cuprous chloride is heated at 105° under pressure for five or six hours, carbamide is formed and copper separates: $CO + 2NH_3 = CO(NH_2)_2 + H_2$ and $Cu_2Cl_2 + H_2 = Cu_2 + 2HCl$. Amines of the methane and benzene series behave in the same manner; aniline, for example, yields diphenylcarbamide. C. H. B.

Oxidation of some Carbamides. By WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1899, **128**, 365—366).—The author has investigated the oxidation of several carbamides by a mixture of normal potassium chromate and sulphuric acid in place of the ordinary chromic mixture. Carbamide yields a small quantity of free nitrogen in addition to carbonic anhydride. Thiocarbamide yields ammonium thiocyanate and, consequently, thiocyanic acid and the products of its

decomposition, together with ammonium sulphate and ammonium hydrogen sulphate, and in some cases small quantities of free nitrogen. Phenylthiocarbamide, diphenylthiocarbamide, methylcarbamide, phenylcarbamide, and diphenylcarbamide do not yield free nitrogen and the diphenyl derivatives are less readily oxidised than the monophenyl derivatives. Benzylcarbamide is oxidised with difficulty, and yields, amongst other products, ammonium sulphate and a small quantity of benzylcarbimide. Phenylcarbamide yields sulphanilic acid and benzonitrile, as well as carbonic anhydride. C. H. B.

Action of Zinc on Ethylic Bromisobutyrate and Furfuraldehyde. Synthesis of β-Furfuryl-α-dimethylethylenelactic Acid. By G. Daïn (*Chem. Centr.*, 1898, i, 884; from *J. russ. chem. Ges.*, **29**, 666—671).—*Ethylic β-furfuryl-α-dimethylethylenelactate*, prepared by dropping a mixture of 95 grams of ethylic bromisobutyrate and 50 grams of furfuraldehyde on to granulated zinc in an apparatus filled with carbonic anhydride, and allowing the product to remain in the dark for 10 days, separates from the fraction boiling at 267—277° in leaflets and sublimes at 293—296° without melting, forming needles. The *sodium* salt, $NaC_9H_{11}O_4$, separates in small, colourless crystals and the *calcium* salt, $Ca(C_9H_{11}O_4)_2 + 3\frac{1}{2}H_2O$, in small, crystalline granules; the *barium* salt is hygroscopic and easily soluble in alcohol.
E. W. W.

Pyrone Group. V. Action of Iodic Acid on Pyromeconic Acid. By Alberto Peratoner and G. Leonardi (*Gazzetta*, 1898, **28**, ii, 297—305).—No definite compounds could be isolated as the result of the action of iodic acid on meconic and comenic acids, but with pyromeconic acid, iodic acid gives iodopyromeconic acid, $C_5H_3O_3I$, and pentiodacetone in the cold, the latter alone being obtained if the solutions are boiling; in both cases, a copious evolution of carbonic anhydride takes place. The pentiodacetone, when decomposed with caustic soda, gave iodoform, sodium carbonate, and sodium iodide in the proportions required by the equation: $C_3HI_5O + 4NaOH = CHI_3 + Na_2CO_3 + 2NaI + H\cdot CHO + H_2O$; formaldehyde was also formed, but no formic acid, the decomposition thus differing from those of the other haloid derivatives of acetone examined by Cloëz. These results do not lead to any definite conclusions as to the position of the substituent groups of the pyrone nucleus in pyromeconic acid. The authors have repeated Brown's experiments (*Annalen*, 1854, **92**, 321) on the action of iodine chloride on pyromeconic acid, but obtained iodoform only, and not the compound to which he assigned the formula $C_3H_4O_3I_8$. T. H. P.

Trimethylene from Trimethylenic Bromide. By Gabriel Gustavson (*Compt. rend.*, 1899, **128**, 437—438).—Trimethylene, prepared by the action of zinc powder and alcohol on carefully purified trimethylenic bromide boiling at 164·5—165°, is almost completely free from propylene. Wolkoff and Menschutkin's conclusion that trimethylene prepared in this way contains about 40 per cent. of propylene, is due to the facts that trimethylenic bromide frequently contains propylenic bromide and that the direct action of trimethylene on

bromine (in which Wolkoff and Menschutkin absorbed the gas) produces a mixture of trimethylenic bromide and propylenic bromide even when the trimethylene is pure. C. H. B.

Conversion of Trimethylene into Propylene. By SIMEON M. TANATAR (*Ber.*, 1899, **32**, 702—705. Compare Abstr., 1896, i, 457). —The author describes in some detail the experiments which led him to adhere to the original statement regarding the conversion of trimethylene into propylene ·(*loc. cit.*), in spite of the criticisms of Wolkoff and Menschutkin (this vol., i, 196). M. O. F.

Constitution and Origin of Naphthenes. By BRUNO BRUHN (*Chem. Zeit.*, 1898, **22**, 900—902).—The author points out that the formation of benzene derivatives from the naphthenes by the action of various reagents is not a proof that these hydrocarbons are derivatives of benzene. Thus the formation of trinitrometaxylene from octonaphthene or of tribromopseudocumene from nononaphthene may be readily explained if it is supposed that these hydrocarbons are derivatives of pentamethylene, and that under the influence of the reagents the ring of five carbon atoms is broken and a new ring of six carbon atoms formed from the chain thus produced. The fact that the most stable saturated ring, C_nH_{2n}, consists of five carbon atoms whilst the most stable unsaturated ring, C_nH_n, contains six carbon atoms is in favour of this view. The new constitution of the naphthenes also agrees much better with the physical properties of these hydrocarbons, as expressed in the curve of boiling points and specific gravities (Markownikoff, *Annalen*, 1898, 301, Anh.). According to Engler's theory, the naphthenes have probably been produced from fatty acids resulting from the hydrolysis of glycerides, and in these circumstances compounds containing the stable five-membered ring would presumably be produced. The naphthenecarboxylic acids are probably formed in a similar manner, a portion of the oxygen being present in the ring. A. H.

Derivatives of Hexahydrometatoluic Acid (1 : 3-Methylcyclo-hexanecarboxylic Acid). By W. SERNOFF (*Chem. Centr.*, 1898, i, 498—499; from *J. russ. chem. Ges.*, **29**, 482—488).—Hexahydrometatoluic acid boils at 239—241°, and does not solidify at a very low temperature. By the action of bromine and red phosphorus, it forms the anhydride of the bromine derivative, which does not solidify on cooling, but after remaining with water for 24 hours and evaporating in a desiccator, yields heavy, monoclinic plates of the α-bromo-acid, $CH_2 {<}^{CH_2-CH_2}_{CHMe\cdot CH_2}{>}CBr\cdot COOH$, which melts at 118°. By heating the bromanhydride with formic acid (1 : 2), the β-bromo-acid, $CH_2 {<}^{CH_2-CH_2}_{CMeBr\cdot CH_2}{>}CH\cdot COOH$, is obtained; it crystallises in triclinic prisms or plates, and melts at 142°. Both acids, when reduced with sodium amalgam, form an oil which, when treated with phosphorus pentachloride and then with aniline, yields the same anilide; this melts at 116°, whilst the anhydride of the original acid melts at 121—122°, and after recrystallising, or by

heating with hydrochloric acid, yields a product which melts at 124°. The author regards the hexahydro-acid obtained by reducing the bromo-acids as one of the isomerides contained in the ordinary hydrogenated acid. By heating the α-bromo-acid with quinoline for an hour at 100°, it loses bromine, and forms an unsaturated liquid acid; this dissolves in water, and easily in light petroleum, decolorises potassium permanganate, and absorbs bromine in carbon bisulphide solution. When heated in alkaline solution on the water-bath, it yields an isomeride, which may also be prepared by removing bromine from the α-bromo-acid; it crystallises from acetone in leaflets or needles, melts at 60—61°, and has the formula $CH_2 \begin{subarray}{c} CH_2 -\!\!- CH \\ \diagup \qquad \diagdown \\ CHMe\cdot CH_2 \end{subarray} C\cdot COOH$. The unsaturated acid, obtained by heating the β-bromo-acid with quinoline at 160—180° for 2 hours, when warmed in alkaline solution at 100°, yields a compound melting at 60—61°, and apparently identical with the compound obtained from the α-acid, but in this case a noncrystallisable acid is formed by heating with alcoholic sodium hydroxide.   E. W. W.

Δ^1-Cycloheptenecarboxylic Acid. By EDUARD BUCHNER (*Ber.*, 1899, **32**, 705—707. Compare Abstr., 1898, i, 301).—Attention has been drawn (*loc. cit.*) to the similarity between suberenecarboxylic (Δ^1-cycloheptenecarboxylic) acid and Einhorn and Willstätter's Δ^1-1-ethylcyclopentene-4-carboxylic acid. Although the amides of these two acids melt at 126° and 130—131° respectively, they are regarded as identical by Willstätter (this vol., i, 26); the author considers it more probable, however, that Einhorn and Willstätter's acid is a cycloheptenecarboxylic acid having the ethylenic group in a different position.   M. O. F.

Properties of Naphthenates and their Qualitative Distinction from Salts of Fatty Acids. By K. CHARITSCHKOFF (*Chem. Centr.*, 1898, i, 1191—1192; from *J. russ. chem. Ges.*, **29**, 691—696).— Naphthenic acids, according to Holde, are obtained by heating neutral petroleum with air in presence of alkali, and Lissenko and Zalosetzky have shown that small quantities are formed when petroleum is distilled. As separated from the crude distillate, these acids have a sp. gr. of 0·961 at 20°, distil without decomposing under 100 mm. pressure, and after repeated distillation are colourless and almost odourless. Although they have the composition of unsaturated compounds, they do not unite with bromine or hydrogen haloids. They dissolve in concentrated sulphuric acid with slight development of heat, and are charred by it after a time. They combine readily with sulphur, especially when warmed, but the sulphur is easily removed by alkali and alcohol. The salts, with the exception of the calcium salt, which crystallises in a fibrous mass, are amorphous; the alkali and silver salts are insoluble in hydrocarbons, the former being easily soluble, but the latter only very slightly so in water; the salts of the alkaline earths are insoluble in hydrocarbons and very slightly soluble in water; those of the heavy metals and of aluminium are very slightly soluble in water, but soluble in hydrocarbons, the iron and copper salts being the most soluble and

the zinc salt dissolving in 20 parts of hydrocarbon. The solution of the faintly blue copper salt in benzene has the intense green colour which is characteristic of the hydrates of copper salts and the white zinc, lead, and mercury salts give a faint yellowish tint to benzene; the last traces of benzene or light petroleum can only be removed from the salts with difficulty, probably on account of the formation of molecular compounds. The solubility of the copper salt in benzene affords a very delicate test for naphthenic acids and their salts, which are often used to adulterate cheap soaps, the copper salt being precipitated with copper sulphate, shaken with benzene, and estimated colorimetrically; small quantities of the copper salts of the fatty acids, however, are also dissolved by the benzene. The copper salts are strong disinfectants, and their use for impregnating wood has been suggested.

<div style="text-align: right">E. W. W.</div>

Action of Potassium Persulphate on Aromatic Hydrocarbons. By C. MORITZ and RICHARD WOLFFENSTEIN (*Ber.*, 1899, **32**, 432—434).— When toluene (2 mols.) is heated with potassium persulphate (1 mol.) in a reflux apparatus at 100° for 3—4 hours, the mixture being stirred constantly, the product contains dibenzyl and benzaldehyde, in addition to unchanged toluene. In a similar manner, dimethyldibenzyl, $CHMePh \cdot CHMePh$, and phenylacetaldehyde were obtained from ethylbenzene.

<div style="text-align: right">C. F. B.</div>

Tertiary Parabutyltoluene and its Derivatives. By ALBERT VERLEY (*Bull. Soc. Chim.*, 1898, [iii], **19**, 67—74).—Tertiary parabutyltoluene (Bialobrzeski, Abstr., 1897, i, 514) is conveniently prepared by gradually adding fuming sulphuric acid (1000 grams) containing 25 per cent. of the anhydride to a mixture of toluene (1000 grams) and isobutylic alcohol (250 grams) kept constantly stirred; its dinitro-derivative melts at 87—88° [Bialobrzeski (*loc. cit.*) gives 94—95°]. When treated with bromine (1 mol.) at 115°, it gives rise to *tertiary parabutylbenzylic bromide*, $CMe_3 \cdot C_6H_4 \cdot CH_2Br$, which strongly irritates the eyes, and is decomposed when distilled; that the bromine atom occupies the position indicated, and has not entered the butyl radicle, appears probable from the fact that neither isobutylbenzene nor di-isobutylbenzene are attacked by bromine. *Tertiary parabutylbenzylic alcohol*, $CMe_3 \cdot C_6H_4 \cdot CH_2 \cdot OH$, prepared from the bromide, boils at 140° under 20 mm. pressure, and has a sp. gr. 0·9282 at 21°; when left in contact for several hours at 60—80° with a mixture of sulphuric acid and fuming nitric acid, it gives rise to *tertiary parabutyldinitrobenzoic acid*, which crystallises from alcohol and, when heated, sublimes without melting. *Tertiary parabutylbenzylic acetate*, $CMe_3 \cdot C_6H_4 \cdot CH_2 \cdot OAc$, has an agreeable odour, boils at 137° under 20 mm. pressure, has a sp. gr. 0·9615 at 0°, and gives rise to the 2 : 5-*dinitro*-derivative, $C_{13}H_6N_2O_6$, which separates from alcohol in straw-coloured crystals and melts at 92·5°. *Tertiary parabutylbenzaldehyde*, $CMe_3 \cdot C_6H_4 \cdot CHO$, boils at 125° under 25 mm. pressure, has a sp. gr. of 0·986 at 0°, smells of bitter almonds, and, in contact with the air, is rapidly oxidised to the *acid*, $CMe_3 \cdot C_6H_4 \cdot COOH$, which melts at 164°; this, when treated with a warm mixture of nitric and sulphuric acids, gives rise to the dinitro-derivative just

described, but is oxidised by boiling dilute nitric acid to terephthalic acid, thus proving that all these compounds are para-derivatives.

When fuming sulphuric acid is added to a mixture of benzene and isobutylic alcohol, it gives rise to tertiary butylbenzene, but there is also formed a considerable quantity of *tertiary dibutylbenzene*, $CMe_3 \cdot C_6H_4 \cdot CMe_3$, which forms massive crystals, melts at 71°, and boils at 116—117° under 20 mm. pressure; it does not react with the usual oxidising agents or chromyl chloride, but yields a *dinitro*-derivative, which melts at 177°. *Tertiary butylparacetylbenzene*, prepared by gradually adding acetic chloride (140 grams) to a mixture of tertiary butylbenzene (400 grams) and aluminium chloride (140 grams) at 0°, boils at 136—138°, has a sp. gr. of 0·9705, a refractive index μ_D 1·518 at 15°, and, on oxidation with dilute nitric acid, gives rise to tertiary parabutylbenzoic acid; it yields no well defined nitro-derivative, but on treating it with bromine and oxidising the product with potassium permanganate, parisobutylphenylglyoxylic acid is obtained.   W. A. D.

NOTE.—In the original paper, many of the compounds are spoken of as isobutyl derivatives, although the formulæ given show that tertiary butyl derivatives are meant.   W. A. D.

Action of Amines on the Bromonitrobenzenes. By NICOLAI N. NAGORNOFF (*Chem. Centr.*, 1898, i, 886—887; from *J. russ. chem. Ges.*, **29**, 699—705).—When bromonitrobenzene is heated with an amine at 183°, derivatives of nitraniline are formed; dipropylpara-nitraniline separates in light-green crystals, melts at 59°, is easily soluble in alcohol, benzene, and acids, and very slightly so in water. In order to determine the effect of the position of the bromine atom, the isomeric bromonitrobenzenes were heated with diethyl-amine, dipropylamine, and diamylamine at 183° for 45 minutes. In each case, there was no reaction with metabromonitrobenzene, and the ortho- was more easily attacked than the para-derivative; with bromine, the ortho-position relatively to the nitro-group is thus the most easily replaceable. By heating orthobromonitrobenzene with triethylamine, the ammonium compound, $NO_2 \cdot C_6H_4 \cdot NEt_3Br$, was obtained, the yield corresponding with 31·6 per cent. of bromine.
                                    E. W. W.

Electrolytic Formation of Nitrobenzene from Orthonitro-benzoic Acid. By CARL SCHALL and R. KLEIN (*Zeit. Elektrochem.*, 1898, **5**, 256—259).—In the fused state, benzoic, salicylic, ortho-bromoparanitrobenzoic, symmetrical dinitrobenzoic, phenylacetic, cinnamic, trichloracetic, pyruvic, malonic, and maleic acids dissolve sodium and potassium carbonates, carbonic anhydride being evolved. Copper benzoate is soluble in fused benzoic acid. These solutions are conductors of electricity, but usually decompose more or less rapidly. Orthonitrobenzoic acid (27·9 grams) takes up 1·3 grams of anhydrous sodium carbonate, and the solution is not decomposed at 200°. With platinum electrodes (12 and 16 square cm. surface and 4·5 mm. apart), 0·8 to 1 ampère and about 29 volts, the formation of nitro-benzene and carbonic anhydride at the anode was observed; the

liquid becomes dark coloured, and carbonaceous masses are also formed, probably owing to reduction of the nitro-acid at the cathode.

T. E.

Action of Acetic Chloride on Phenylic Acetate in Presence of Aluminium Chloride. Preparation of Paracetophenylic Acetate. By ALBERT VERLEY (*Bull. Soc. Chim.*, 1898, [iii], 19, 140).—When acetic chloride (1 mol.) is added, drop by drop, to a mixture of phenylic acetate (3 mols.) with aluminium chloride (1 mol.) under diminished pressure, and the product subsequently distilled, a substance is obtained which boils at 160° under 22 mm. pressure, and forms brilliant, white crystals melting at 54°. This compound is evidently paracetophenylic acetate, since it is oxidised by boiling with dilute nitric acid to parahydroxyacetobenzoic acid melting at 185°, and yields, on hydrolysis, parahydroxyacetophenone melting at 110°.

N. L.

Orthonitrobenzylic Chloride and Paranitrobenzylic Chloride. By JOHANNES THIELE and OTTO DIMROTH (*Annalen*, 1899, 305, 102—123).—*Orthonitrobenzylic methylic ether*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot OMe$, prepared by reducing orthonitrobenzylic chloride in methylic alcohol with sodium, is a yellow, viscous oil having a faint odour of nitrobenzene; it boils at 130—132° under 15 mm. pressure, and has a sp. gr. of 1·2049 at 15°/4°. The *ethylic* ether boils at 167—172° under 50 mm. pressure.

Orthamidobenzylic methylic ether, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot OMe$, cannot be prepared by the action of acidic reducing agents on the nitro-compound, and is best obtained by means of caustic soda and ferrous sulphate; it is a colourless oil which rapidly becomes brown when exposed to air, and gives the reaction for aniline with bleaching powder. The ether boils at 123—124° under 30 mm. pressure, and has a sp. gr. of 1·0499 at 17°/4°; the *oxalate* melts at 124°. The *ethylic* ether boils at 123—129° under 25 mm. pressure; the *hydrochloride* and *oxalate* melt at 82—83° and 136° respectively.

Orthohydroxybenzylic methylic ether, $OH \cdot C_6H_4 \cdot CH_2 \cdot OMe$, is a limpid oil having the odour of guaiacol, and boils at 128—130° under 40 mm. pressure; when distilled under atmospheric pressure, it becomes completely converted into resin, and as it has not the odour of coffee, it differs considerably from the caffeol of Bernheimer, which he regarded as the methylic ether of saligenin. The *ethylic* ether boils at 111—113° under 20 mm. pressure, and has the odour of cresol.

Phenylic orthonitrobenzylic ether, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot OPh$, prepared from orthonitrobenzylic chloride, phenol, and alcoholic potash, crystallises from alcohol in slender, lustrous prisms and melts at 63°.

Phenylic orthamidobenzylic ether, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot OPh$, crystallises from alcohol and melts at 81—82°.

Orthamidophenylic orthamidobenzylic ether,

$$NH_2 \cdot C_6H_4 \cdot CH_2 \cdot O \cdot C_6H_4 \cdot NH_2,$$

obtained by reducing orthonitrophenylic orthonitrobenzylic ether (Lellmann and Mayer, Abstr., 1893, i, 198), crystallises from alcohol in white prisms and melts at 118°.

When paranitrobenzylic chloride is reduced with stannous chloride,

and the alkaline liquid saturated with hydrogen sulphide, **paradi-amidobenzylic sulphide** is produced; further reduction with zinc dust gives rise to paratoluidine. If the reduced liquid is made alkaline, and oxidised with ammonium persulphate, the *stanno*-compound, $C_7H_9NSnO_2$, is formed; it is insoluble in ether, alcohol, and chloroform, but dissolves readily in aniline, phenol, and glacial acetic acid.

Diamidodibenzylic bisulphide, $C_{14}H_{16}N_2S_2$, prepared by the action of hydrogen sulphide on paradiamidobenzylic alcohol (compare O. Fischer and G. Fischer, Abstr., 1895, i, 343), melts at 96—98°; the *hydrochloride* crystallises in slender needles, and the *acetyl* derivative melts at 173—174°. When paradiamidobenzylic alcohol is reduced with stannous chloride, paratoluidine is formed.

Orthonitrobenzylic chloride, when reduced with stannous chloride and treated with hydrogen sulphide, yields orthodiamidobenzylic sulphide (compare Gabriel and Posner, Abstr., 1895, i, 190).

M. O. F.

Absorption of Oxygen by Potassium Pyrogallol. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1898, [vii], 15, 294—320).—An account of work already published. (Compare Abstr., 1899, i, 645; ii, 534.) G. T. M.

Aromatic Allylic and Propenylic Ethers. By CHARLES MOUREU (*Ann. Chim. Phys.*, 1898 [vii], 15, 115—144).—This work has already been published. (Compare Abstr., 1896, i, 215, 477, 646; 1897, i, 336, 403; 1898, i, 411, 518, 644, 660; this vol., i, 30, 125, 138.) G. T. M.

Derivatives of Guaiacol. By STEFANO DI BOSCOGRANDE (*Real. Accad. Linc.*, 1897, ii, 33—35, 306—307).—*Bromethoxyguaiacol*, $OMe \cdot C_6H_4 \cdot O \cdot C_2H_4Br$, obtained by heating a solution of guaiacol in alcoholic potash with an excess of ethylenic bromide, crystallises in long, colourless needles melting at 49°, and soluble in ordinary organic solvents. *Bromethoxytrinitroguaiacol*, $OMe \cdot C_6H(NO_2)_3 \cdot O \cdot C_2H_4Br$, formed by the action of cold nitric acid on the preceding compound, crystallises from boiling alcohol in very minute, yellow needles melting at 120°. *Diguaiacylic ethylenic ether*, $C_2H_4(O \cdot C_6H_4 \cdot OMe)_2$, obtained by the action of bromethoxyguaiacol on guaiacol, or by treating the latter with a moderate quantity of ethylenic bromide, crystallises from boiling alcohol in large, lustrous, white needles melting at 130°. *Phenylic guaiacylic ethylenic ether*, $OMe \cdot C_6H_4 \cdot O \cdot C_2H_4 \cdot OPh$, from bromethoxyguaiacol and potassium phenoxide, crystallises in beautiful, silky needles melting at 75°. *Triguaiacylic phosphate*, $PO(O \cdot C_6H_4 \cdot OMe)_3$, obtained by the action of phosphorus pentachloride on guaiacol in benzene solution, crystallises in white prisms melting at 91°.

Guaiacol picrate, $OH \cdot C_6H_4 \cdot OMe, C_6H_3N_3O_7$, crystallises in minute, orange-red needles melting at 80° and very soluble in water and the ordinary solvents; it slowly decomposes on exposure to diffused light, the colour changing from red to yellow, whilst the melting point is raised. Picric acid is precipitated when light petroleum is added to the benzene solution of the picrate. *Benzyl-*

guaiacol, $CH_2Ph\cdot C_6H_3(OH)\cdot OMe$, obtained by the action of benzylic chloride on guaiacol in the presence of metallic zinc, is a fluorescent, pale yellow liquid boiling at 269—270° under a pressure of 436 mm. and having a sp. gr. of 1·138 at 13°. N. L.

Action of Mercuric Salts on Aromatic Compounds. By OTTO DIMROTH (*Ber.*, 1899, **32**, 758—765. Compare this vol., i, 54). —All mercuric salts, such as the acetate, sulphate, and nitrate, which are decomposed by excess of water, are capable of acting on aromatic compounds, but the chloride only acts slightly even in presence of sodium acetate, and the cyanide does not act at all. The separation of thiophen from benzene, which was partially effected by Volhard (Abstr., 1892, 828) by means of mercuric chloride and sodium acetate, is readily brought about by means of mercuric sulphate (Denigès, Abstr., 1895, i, 411), nitrate, or acetate; in the latter case, the chief product is *thiophen dimercuric hydroxyacetate*, $OH\cdot Hg\cdot C_4H_2S\cdot Hg\cdot OAc$, which separates as a crystalline powder, and decomposes without melting at 270°; when dissolved in acetic acid, slender needles of the *diacetate* are slowly deposited; sulphuric acid and isatin give an intense indophenin reaction with the hydroxyacetate, and hydro-chloric acid decomposes it into thiophen and mercuric chloride.

Benzene is only slightly attacked by aqueous mercuric acetate at 80°, but at 110—120° it gives phenylmercuric acetate (this vol., i, 54) together with *phenylene dimercuric diacetate*, $C_6H_4(Hg\cdot OAc)_2$, which is insoluble in benzene, separates as a powder from acetic acid, and melts at about 230°. Mercuric sulphate and nitrate behave similarly, but mercuric chloride is only slightly acted on by benzene even in presence of sodium acetate.

With mercuric acetate, toluene gives a mixture of salts from which sodium chloride precipitates orthotolylmercuric chloride, $C_6H_4Me\cdot HgCl$, melting at 140—142° (Michaelis and Genzken, Abstr., 1888, 146) and paratolylmercuric chloride melting at 230—231° (Otto, *J. pr. Chem.*, 1865, **1**, 185); these were separated by fractional crystallisation, and their identity was further proved by conversion into bromotoluene.

When acted on by an excess of phenol, mercuric sulphate, nitrate and acetate are no longer precipitated by sodium hydroxide, but from an acid solution, hydroxyphenylmercuric salts are slowly deposited; mercuric chloride is only slightly attacked, but a mixture of chlorides is precipitated by sodium chloride from the product of the action of the sulphate, nitrate, and acetate. *Orthohydroxyphenylmercuric chloride*, $HO\cdot C_6H_4\cdot HgCl$, is soluble in cold alcohol and melts at 152·5°, whilst the *benzoate* crystallises from alcohol in slender needles and melts at 204°. *Parahydroxyphenylmercuric chloride* is soluble in boiling alcohol, crystallises from acetone in glistening flakes, and melts at 224—225°; the *benzoate* crystallises from ethylic benzoate in glistening flakes and melts at 275—276°. *Hydroxyphenyldimercuric dichloride*, $HO\cdot C_6H_3(HgCl)_2$, is almost insoluble in all solvents, and melts at 258°; the *benzoate* is an insoluble white powder. The substance described by Grützner (this vol., i, 198) as parahydroxyphenyl-mercuric chloride is a mixture of the three chlorides just described,

By the action of methylic iodide, the corresponding anisylmercuric iodides are produced. The action of ethylic iodide on orthohydroxyphenylmercuric chloride gives orthophenetylmercuric iodide and *orthomercuric diphenetyl*, $Hg(C_6H_4 \cdot OEt)_2$; this crystallises from alcohol in needles and melts at 83°; it differs from the substance melting at 224° which was described by Michaelis (Abstr., 1894, i, 191), but its constitution is proved by the formation of orthophenetylmercuric chloride (m. p. 132°) by the action of alcoholic mercuric chloride, of the acetate (m. p. 150°) by the action of glacial acetic acid, and of phenetoil and mercuric chloride by the action of hydrochloric acid. From an alkaline solution of orthohydroxyphenylmercuric chloride, carbonic anydride precipitates *orthophenylmercuric oxide*, $C_6H_4 <^O_{Hg}$, as a white powder, which is only slightly soluble in most organic solvents, but dissolves readily in phenol, in which it has a normal molecular weight according to the cryoscopic method. This substance is analogous to the orthotrimethylphenol ammonium, $C_6H_4 <^O_{NMe_3}$, described by Griess (Abstr., 1880, 636, 637); parahydroxyphenylmercuric chloride and hydroxyphenylenedimercuric dichloride give similar precipitates, but these were not obtained free from chlorine.

Catechol and quinol are oxidised by mercuric salts, but resorcinol and phloroglucinol give mercuric compounds, as also do the phenylic ethers, benzoic and salicylic acids, naphthalene and the naphthols, phenanthrene, anthracene, and aromatic amines (Pesci, Abstr., 1898, i, 648). T. M. L.

Action of Titanium Chloride on Organic Compounds. By ANDRÉ KLING (*Bull. Soc. Chim.*, 1898, 19, [iii], 190).—Aniline, free from toluidine, when dissolved in chloroform or benzene and treated in the cold with titanium chloride, yields a colouring matter of the rosaniline type which leaves a notable amount of titanium oxide on ignition. When the experiment is performed at high temperatures in the absence of solvents, a colouring matter of the violaniline series is produced. It is suggested that the former product is a rosaniline containing an atom of titanium, replacing the methane carbon atom of pararosaniline, and that the compound is decomposed by heat into the violaniline derivative. When anisoil is treated in a similar manner, it yields methylic chloride and phenylic orthotitanate.
G. T. M.

Reactions of Mercurio-aniline. By G. MONTECCHI (*Gazzetta*, 1898, 28, ii, 434—436).—Thiourea and mercurio-aniline, when ground together in molecular proportion, readily react with the separation of mercuric sulphide and formation of dicyanodiamide.

When diphenylthiourea and mercurio-aniline, in molecular proportion, are intimately mixed in presence of a small quantity of aqueous aniline, a rise of temperature occurs, accompanied by the production of a black, pasty mass, which, on extraction with boiling alcohol, yields triphenylguanidine. T. H. P.

Compounds of Mercury with Organic Bases. By LEONE
PESCI (*Gazzetta*, 1898, **28**, ii, 436—477).—The author gives a sum-
mary of the results obtained by himself and his pupils in their work
on this subject during the period 1892—1898 (see Abstr., 1890,
1211; 1891, 268; 1892, 1448; 1893, i, 24, 304, 322; 1894, i, 248,
249; 1895, i, 357, 358; 1896, i, 186, 388; 1897, i, 36, 328, 337, 370,
559; this vol., i, 361, and preceding abstract).   T. H. P.

**Reaction of Orthodiazobenzoic Acid with Sulphurous Acid
and Copper Powder.** By WILLIAM E. HENDERSON (*Amer. Chem. J.*,
1899, **21**, 206—210).—When a solution of orthodiazobenzoic acid
sulphate is added to a cold saturated solution of sulphurous anhy-
dride in which copper powder is suspended, nitrogen is evolved. A
considerable amount of copper passes into solution, part of the sul-
phurous acid is oxidised to sulphuric, and, instead of orthosulpho-
benzoic acid, the chief product is dithiosalicylic acid (List and Stein,
Abstr., 1898, i, 697), the yield being about 50 per cent. of the
theoretical.   J. J. S.

Salts of Benzylidenehydrazinesulphonic Acid. By ROBERT
STOLLÉ (*Ber.*, 1899, **32**, 799—800).—If the product obtained by the
interaction of anhydrous hydrazine with potassium pyrosulphate is
neutralised with aqueous potassium carbonate, extracted with
benzaldehyde, filtered, dried in a vacuum and extracted with a large
quantity of hot alcohol, *potassium benzylidenehydrazinesulphonate*,
$CHPh{:}N{\cdot}NH{\cdot}SO_3K$, crystallises from the solution on cooling; it
forms glistening leaflets, readily taking up water and forming
benzaldehyde and potassium hydrazinesulphonate. It reduces
ammoniacal silver solution on warming, and is completely decomposed
by mineral acids into benzaldehyde, hydrazine, and sulphuric acid. On
the addition of barium chloride, its solution becomes coloured an
intense yellow and gradually deposits a rose coloured powder
probably having the constitution $(CHPh{:}N{\cdot}NH{\cdot}SO_3{\cdot}Ba{\cdot})_2O$.

Potassium hydrazinesulphonate reduces ammoniacal silver nitrate
in the cold.   J. F. T.

Acetanilide and Hypochlorites. By NICOLA CASTORO (*Gazzetta*,
1898, **28**, ii, 312—316).—By the action of bleaching powder on a
solution of acetanilide acidified with acetic acid, Bender (Abstr., 1887,
44) obtained the compound, $Ph{\cdot}NClAc$, melting at 91°. The author
has been unable to isolate this substance, but finds that the reaction
of the two substances mentioned always gives rise to parachloracetan-
ilide and 1 : 4-dichloracetanilide in proportions depending on the relative
quantities of acetanilide, hypochlorite, and acetic acid employed.
                                                           T. H. P.

[NOTE.—Bender's statement is correct, and the compound has been
obtained frequently in the laboratory of the Central Technical College,
London.—EDITOR].

**Action of Sulphuric Acid on Symmetrical Aromatic
Carbamides.** By PAUL CAZENEUVE and MOREAU (*Bull. Soc. Chim.*,
1898, [iii], **19**, 21—25).—When symmetrical diphenylcarbamide is

warmed with sulphuric acid of sp. gr. 1·711 at a temperature not exceeding 110°, it gives rise to the *compound*, $COOH \cdot NH \cdot C_6H_4 \cdot SO_3H$, which is decomposed, on further heating, into carbonic anhydride and sulphanilic acid. Symmetrical diparatolylcarbamide does not yield the intermediate carboxylic compound, but at 150—160° gives rise to a mixture of paratoluidine-ortho- and -meta-sulphonic acids. Symmetrical diorthotolylcarbamide, under similar treatment, yields orthotoluidine-3-sulphonic acid, whilst dimetaxylylcarbamide gives a product apparently identical with 4-metaxylidine-6-sulphonic acid (Jacobsen and Ledderboge, Abstr., 1883, 593). Di-ψ-cumylcarbamide (Abstr., 1897, i, 519) gives rise to no definite product, whilst dixylylcarbamide [$Me_2 : NH = 1 : 2 : 4$] yields a new *4-orthoxylidine-sulphonic acid*, which probably contains the sulpho-group in position 6. The action of sulphuric acid on the symmetrical carbamides derived from 3-orthoxylidine and 2-paraxylidine is being studied.

W. A. D.

Rearrangement of Imido-ethers. By HENRY L. WHEELER and T. B. JOHNSON (*Amer. Chem. J.*, 1899, 21, 185—193).—It is suggested that formethylanilide is produced from phenyl formimidoethylic ether (this vol., i, 354) by the addition and subsequent loss of ethylic iodide, a view which finds support from the fact that benzimidoethylic ether, $OEt \cdot CPh\colon NH$, when heated at 100° with ethylic iodide, yields ethyl-benzamide, $COPh \cdot NHEt$. This reaction was studied quantitatively, and, in addition to ethylbenzamide, benzamide, benzonitrile, and cyaphenin were isolated in relatively small amounts. These are the first cases observed in which a silver salt of an acylic amide, anilide, or imido-ether gives alkylic derivatives of this type with alkylic iodides. Formethylanilide boils at 259—266° under 772 mm. pressure, the boiling point being 258° under 728 mm. pressure, according to Pictet and Crépieux (Abstr., 1888, 688). Ethylbenzamide boils at 298—299°, and not at 256—260°, as Schmidt and Gattermann state (Abstr., 1887, 358). J. J. S.

Azonium Chromogenes. By W. SCHAPOSCHNIKOFF (*Chem. Centr.*, 1898, i, 722—723 ; from *J. russ. chem. Ges.*, 29, 535—565. Compare Abstr., 1897, i, 172, 491).—The author arrives at the following conclusions : (1) Aposafranine and induline are amido-derivatives of azonium bases, and can be converted into these bases by diazo-tising, &c. ; (2) the azonium bases are strong bases, and even form carbonates ; (3) the behaviour and properties of the azonium bases are very similar to those of the acetyl derivatives of aposafranine and rosinduline ; (4) the azonium bases give substitution reactions which have hitherto been considered characteristic of the ortho-quinones ; (5) phenylphenazonium and phenylnaphthazonium are the chromogenes of the safranines and the indulines.

Acetylaposafranine carbonate, obtained by passing dry carbonic anhydride into the ethereal solution of the base, forms brown crystals, and is decomposed by water. Phenylphenazonium is best isolated as the double salt with ferric chloride ; the dichromate, $(C_{18}H_{13}N_2)_2Cr_2O_7$,

forms a dark violet precipitate, or crystallises from water in yellow prisms; the platinochloride, $C_{18}H_{13}N_2PtCl_6$, is an almost insoluble microcrystalline powder; the aurichloride, $C_{18}H_{13}N_2AuCl_4$, is a yellow powder; the mercurichloride, $C_{18}H_{13}N_2HgCl_3$, forms an orange-yellow precipitate, and is very slightly soluble in water, and the picrate a brownish-red precipitate which crystallises from water in slender needles. A good yield of aposafranone, $C_6H_3O\ll^{N-}_{NPh}>C_6H_4$, is obtained by decomposing the ferric chloride compound of phenyl-phenazonium with a dilute solution of sodium hydroxide in alcohol, filtering the ferric hydroxide, acidifying, passing air through the warm solution, precipitating with sodium acetate, and finally crys-tallising from benzene.

Dimethylaposafranine, $NMe_2 \cdot C_6H_3 \ll^{N-}_{NPhCl}>C_6H_4$, prepared by the action of dimethylamine on the ferric chloride compound of phenyl-phenazonium dissolved in alcohol, air being passed through the mixture, crystallises from water in thick prisms, and gives a violet solution in alcohol which is not fluorescent; the platinochloride and chromate are very slightly soluble microcrystalline powders.

Phenylaposafranine (anilinophenylphenazonium),

$$NHPh \cdot C_6H_2(NH_2) \ll^{NPhCl}_{N-}>C_6H_4,$$
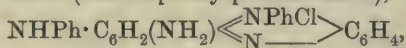
is obtained by the action of aniline on an alcoholic solution of the ferric chloride compound of phenazonium, air being passed through the mixture. The hydrochloride crystallises in dark blue prisms, and dyes wool and silk heliotrope.

Anilinophenylaposafranine, $C_6H_2(NHPh)_2 \ll^{NPhCl}_{N-}>C_6H_4$,   pre-pared by the action of 7 parts of aniline on 1 part of phenazonium, separates in dark green crystals, gives a red solution in alcohol, but is insoluble in water.

Dimethylrosinduline, $C_6H_4 \colon C_6H(NMe_2) \ll^{N-}_{N(NO_3)Ph}>C_6H_4$,   pre-pared from phenylnaphthaphenazonium in the same way as the corre-sponding safranine is obtained from the corresponding phenazonium, crystallises in green leaflets from water containing a little acid, and dyes wool and silk carmin red; the reddish-violet platinochloride and the dark red chromate are very slightly soluble. Rosindone is pre-pared in a similar manner to aposafranine. Naphthaphenosafranine, prepared by the action of ammonia on acetylmonamidophenyl-naphthaphenazonium, resembles phenosafranine in its behaviour and the properties of its salts and derivatives; it separates in dark green crystals and is easily soluble in water, forming a cherry-red solution with orange-yellow fluorescence. By methods of preparation similar to that of naphthaphenosafranine, the following compounds may be obtained: anilinonaphthaphenosafranine, which dyes silk bluish-green; a piperidine derivative which dyes wool and silk rose, resembling in shade that of Magdala red, and a metatoluylenediamine derivative, which dyes wool and silk mauve.   E. W. W.

Nitracetophenone and Nitracetone. By AD. LUCAS (*Ber.*, 1899, **32**, 600—607. For other nitroketones compare Hollemann, Abstr., 1897, i, 599 ; and also Trans., 1898, **73**, 991, and 1899, **75**, 211).—*α-Iodacetophenone*, COPh·CH₂I, melts at 28°, and has an irritating odour similar to that of the bromo-compound ; in ethereal solution, it gradually decomposes, with liberation of iodine. *α-Isonitroacetone* is produced, together with a substance melting at 205°, by the action of silver nitrite on α-iodacetophenone ; it crystallises from ether and melts at 108°. It is easily soluble in ether, alcohol, and benzene, slightly soluble in cold water, and on cooling separates in fine needles from an aqueous solution saturated at 30° ; the aqueous solution, however, decomposes slowly in the cold, and rapidly if heated above 30° ; the alcoholic solution decomposes yet more rapidly, with formation of ethylic benzoate and nitrous acid ; the solid is stable in dry air. The aqueous solution is acid to litmus, and gives a faint colour with ferric chloride, which gradually deepens to an intense reddish-brown ; the same colour appears immediately in ethereal solution. The substance is soluble in caustic soda and in sodium carbonate, giving a neutral sodium salt, from which it is precipitated again unchanged by the addition of acids. The ammonium salt is precipitated by dry ammonia from a solution of the substance in dry ether or benzene, but phosphorus pentachloride and acetic chloride have no action on an anhydrous solution. The salts give an immediate coloration with ferric chloride, which disappears more rapidly than is the case with the free acid, owing to decomposition into a benzoate and nitrous acid ; a similar decomposition is effected immediately by concentrated sulphuric acid.

Ammonium-isonitracetone is a white salt which decomposes in the desiccator, becoming orange-red in colour, and giving off a strong odour of mice ; the orange-yellow solution gives a deep red-brown coloration with ferric chloride, which does not appear again, as the products of decomposition are nitrous acid and red ferric acetate. *Nitracetone* was obtained as a yellow oil* smelling slightly of acetic acid ; its aqueous solution is acid, and gives an immediate reddish-brown coloration with ferric chloride, but only gradually acts on a solution of starch and potassium iodide. With hydroxylamine, nitracetone forms a salt, but not an oxime, and nitracetophenone behaves in the same way. The colourless liquid, boiling at 152°, which was prepared by L. Henry and de Battice (*Bull. Acad. Roy.Belg.*, [iii], **36**, 149) by the oxidation of nitroisopropylic alcohol, and described by them as nitroacetone, is regarded by the author as an entirely different substance.

T. M. L.

Orthohydroxyphenoxyacetone. By CHARLES MOUREU (*Compt. rend.*, 1899, **128**, 433—435. Compare this vol., i, 125).—*Orthohydroxyphenoxyacetone*, OH·C₆H₄·O·CH₂·COMe, obtained by the action of chloracetone on monosodiumcatechol, forms brilliant white, long, slender needles which melt at 98—99° and dissolve in alcohol, ether, or boiling water, but are only slightly soluble in cold water. It boils at 169—170° under 46 mm. pressure, and is only slightly volatile in

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* This is probably a mixture of nitracetone and isonitracetone in equilibrium, similar to those produced by fusing other nitroketones.—T. M. L.

steam, gives no reaction with ferric chloride, but reduces ammoniacal silver nitrate. The acetate, $OAc \cdot C_6H_4 \cdot O \cdot CH_2 \cdot COMe$, boils at 176—180° under 19 mm. pressure; the phenylhydrazone melts at 113°, and the oxime, which crystallises in small prisms, at 76—77°.

By interaction with a mixture of alcohol and ethylic imidoformate hydrochloride (which produces ethylic orthoformate), the orthohydroxy-phenoxyacetone yields the acetal, $OH \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CMe(OEt)_2$, and this, when heated, splits up into alcohol and ethoxymethylethane-catechol, $C_6H_4 \begin{matrix} O \cdot CH_2 \\ O \cdot CMe \cdot OEt \end{matrix}$, a colourless, odourless, neutral, oily liquid, which boils at 124—125° under 15 mm., and at 233—237°, with partial decomposition, under ordinary pressure, is volatile in steam and has a sp. gr. of 1·1271 at 0°. When boiled with dilute sulphuric acid, it yields alcohol and orthohydroxyphenoxyacetone. C. H. B.

Aromatic Ketones containing Iodine. By A. COLLET (*Compt. rend.*, 1899, **128**, 312—313).—*Phenyl iodomethyl ketone*, $CH_2I \cdot COPh$, prepared by warming an alcoholic solution of phenyl chloromethyl ketone at 45—50° for 2 hours with finely powdered potassium iodide, crystallises from alcohol in colourless needles, and melts at 29·5—30°; on oxidation with hot alkaline potassium permanganate, it yields benzoic acid, whilst when warmed with lead hydroxide suspended in water, it forms benzoylcarbinol.

Paratolyl iodomethyl ketone, $C_7H_7 \cdot CO \cdot CH_2I$, prepared from para-tolyl chloromethyl ketone, forms colourless needles, melts at 40—41°, and on oxidation yields terephthalic acid; alcoholic potassium acetate converts it into paratoluoylcarbinyl acetate, which melts at 83°.

Paratolyl iodethyl ketone, $C_7H_7 \cdot CO \cdot CHMeI$, crystallises from alcohol in colourless, lustrous plates, melts at 102—103°, and on oxidation with warm alkaline potassium permanganate yields paratoluic and terephthalic acids; alcoholic potassium acetate converts it into methylparatoluoylcarbinyl *acetate*, $C_7H_7 \cdot CO \cdot CHMe \cdot OAc$, which melts at 106°.

These ketones are acted on by light, iodine being liberated, and their vapours strongly irritate the eyes. W. A. D.

Application of Friedel and Craft's Method of Synthesis in the Preparation of Aromatic Aldehydes and Ketones under Reduced Pressure. By ALBERT VERLEY (*Bull. Soc. Chim.*, 1898, [iii], **19**, 137—140. Compare this vol., i, 207).—In reply to Bouveault (*Bull. Soc. Chim.*, [iii], **17**, 1020), the author contends that, although some loss undoubtedly occurs when operating under reduced pressure with volatile compounds, like acetic chloride, or with such as dissociate, like ethylic cymylglyoxalate, yet the method described by him is, as a rule, attended with considerable advantages. In the preparation of *isobutyrylparacymene*, a liquid of sp. gr. 0·957 at 0°, and boiling at 152° under 20 mm. pressure, or at 260—262° under atmospheric pressure, the yield is 97 per cent., and an almost theoretical yield is also obtained in the case of *acetothymylic methylic ether*, which boils at 155° under 20 mm. pressure. The boiling point of ethylic cymylglyoxalate is 186° under 21 mm. pressure, and not 130—132° as

was previously stated through a clerical error. With regard to the objections raised against the use of bromine, the author finds that substitution always takes place in the side chain of ketones, and not in the aromatic nucleus. Should the latter case occur, however, the difficulty would be obviated by the use of chloracetic chloride instead of acetic chloride. N. L.

Formation of Ketones with the aid of Aluminium Chloride. By J. BOESEKEN (*Bull. Soc. Chim.*, 1898, [iii], **19**, 349—350).—In the preparation of ketones by the interaction of aromatic hydrocarbons with aliphatic acid chlorides, almost theoretical yields are obtained if care is taken that the aluminium chloride, freshly prepared, is always in excess, and that the reaction does not extend over too long a time. The temperature may conveniently be that of boiling carbon bisulphide, at which hydrogen chloride is regularly evolved, and operating under reduced pressure, as proposed by Verley (preceding abstract) is unnecessary. The large yields obtained by the latter method are attributed to the fact that the arrangement of the apparatus for working in a vacuum necessitates the presence of an excess of aluminium chloride during the greater part of the reaction. By the gradual addition of a mixture of phenetoil (50 grams) with acetic chloride (50 grams) to 100 grams of aluminium chloride covered with a layer of boiling carbon bisulphide, 64·3 grams of parethoxyphenyl methyl ketone were obtained—a yield of nearly 96 per cent. of the theoretical. N. L.

Action of Aniline on Dinitrophenyldiacetylmethane. By FERNAND MUTTELET (*Bull. Soc. Chim.*, 1898, [iii], **19**, 74).—When dinitrophenyldiacetylmethane (this vol., i, 281) is heated with aniline (1 mol.) for 8 hours at 100—105°, it gives rise to acetanilide together with *dinitrophenylacetylmethane*, $CH_2Ac \cdot C_6H_3(NO_2)_2$, which crystallises from alcohol in lustrous leaflets, and melts at 73—75°. W. A. D.

New Method of Preparing α-Methylcinnamic Acid from β-Phenyl-α-methylethylenelactic Acid. By G. DAÏN (*Chem. Centr.*, 1898, i, 674—675; from *J. russ. chem. Ges.*, **29**, 607—614).—α-Methylcinnamic acid is prepared by heating β-phenyl-α-methylethylenelactic acid (1 mol.) with acetic chloride or acetic anhydride (2 mols.) at 100—180° for 12—20 hours. The calcium salt, $Ca(C_{10}H_9O_2)_2 + 3H_2O$, crystallises in slender needles, is easily soluble in hot and very soluble in cold water; the silver salt, $AgC_{10}H_9O_2$, crystallises in feathery clusters, and the barium salt in small prisms. The stereoisomeric acid,
$$\begin{array}{c} Ph \cdot C \cdot H \\ \| \\ COOH \cdot C \cdot Me \end{array}$$
obtained from the salts, crystallises from ether in monoclinic prisms and melts at 81—82°. When recrystallised from light petroleum, it is partially converted into the more stable isomeride,
$$\begin{array}{c} Ph \cdot C \cdot H \\ \| \\ Me \cdot C \cdot COOH \end{array}$$
which is also formed by distilling methylcinnamic acid, and crystallises in long, flexible needles melting at 74°. By the action of concentrated sulphuric acid at 120° for 6 hours, α-methylcinnamic acid yields allylbenzene and methronene. E. W. W.

Action of Zinc on Ethylic α-Bromopropionate and Benzaldehyde (Synthesis of β-Phenyl·α-methylethylenelactic Acid). By G. Daïn (*Chem. Centr.*, 1898, i, 668 ; from *J. russ. chem. Ges.*, **29**, 597—607).—Ethylic β-phenyl-α-methylethylenelactate is prepared by the action of ethylic α-monobromopropionate (50 grams) on benzaldehyde (31 grams) in presence of granulated zinc. The intermediate bromo-zinc compound formed in this reaction, when boiled with absolute alcohol or water, also yields the ethylic salt. The acid, obtained by hydrolysing the ethylic salt with baryta water, crystallises from light petroleum ; the *sodium* salt, $C_{10}H_{11}O_3Na + 2H_2O$, crystallises from water ; the *calcium* salt crystallises with $4H_2O$; the *barium* salt, $Ba(C_{10}H_{11}O_3)_2 + 3\frac{1}{2}H_2O$, crystallises in needles or prisms ; the *zinc* salt, $Zn(C_{10}H_{11}O_3)_2 + H_2O$, crystallises in needles ; the *silver* salt, $AgC_{10}H_{11}O_3$; the *ammonium* salt crystallises in long, slender, matted needles ; the *lead* salt forms scales which become nodular after prolonged digestion with water ; the *copper* salt is very soluble in ether and alcohol and soluble in water.

E. W. W.

Action of Zinc on Ethylic Bromisovalerate and Benzaldehyde. By G. Daïn (*Chem. Centr.*, 1898, i, 884—885 ; from *J. russ. chem. Ges.*, **29**, 659—666).—*Ethylic β-phenyl-α-isopropylethylenelactate* is prepared by dropping a cooled mixture of benzaldehyde (51 grams) with ethylic bromisovalerate (105 grams) on to granulated zinc, allowing the product to remain 4 days, and then acidifying with dilute sulphuric acid ; it forms a viscous liquid with an odour recalling that of pineapple. The acid, obtained by hydrolysing the ethylic salt with baryta water, crystallises in slender needles from a mixture of light petroleum and benzene, melts at 106—107°, is easily soluble in ether, alcohol, ethylic acetate, and acetic acid, very slightly soluble in light petroleum and benzene, and is volatilised by steam ; 100 parts of water at 18° dissolve 4·79, and at 100°, 4·83 parts of acid. The *calcium* salt, $Ca(C_{12}H_{15}O_3)_2$, forms white crystals, the *sodium* salt, $NaC_{12}H_{15}O_3 + 4H_2O$, nodules, and the *barium* and *potassium* salts are very hygroscopic. The *silver* salt, $AgC_{12}H_{15}O_3$, is formed as a white, amorphous precipitate which dissolves in hot water, but does not separate again on cooling. Only a small portion of the acid distils unchanged at 201—210°, the greater part decomposing into carbonic anhydride, water, and phenylpropylethylene, CHPh:CHPr. By the action of sulphuric acid on the acid, phenylpropylethylene and small quantities of isovaleric and benzoic acids are formed ; the latter acid is derived from the benzaldehyde.

E. W. W.

Oxidation of Phenylhydroxypivalic Acid. By G. Daïn (*Chem. Centr.*, 1898, i, 889 ; from *J. russ. chem. Ges.*, **29**, 656—659).—When 3 grams of potassium permanganate in 2 per cent. solution are added in small portions to 5·4 grams of potassium phenylhydroxypivalate in 2 per cent. solution at the ordinary temperature, benzaldehyde and potassium isobutyrate are first formed and are then oxidised to potassium benzoate and potassium α-hydroxyisobutyrate.

E. W. W.

Hydroxyphenylglyoxylic Acids. Synthesis of Vanillin. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1898, [iii], 19, 75—77).—When paramethoxyphenylglyoxylic acid is heated with 30 per cent. aqueous caustic potash for 12 hours at 170°, it is converted into *parahydroxyphenylglyoxylic acid*, which, on adding benzene to the ethereal solution, separates in hard, lustrous crystals melting at 172—173°. Veratroylcarboxylic acid, when similarly treated, is partially resolved into vanilloyl- and catechoyl-carboxylic acids; on boiling the crude product for 1 hour with dimethylaniline (compare Gassmann, Abstr., 1897, i, 343), subsequently with 10 per cent. sulphuric acid, and finally extracting with ether, vanillin is obtained along with veratric aldehyde. On shaking the ethereal solution with aqueous sodium carbonate, the vanillin alone is removed, and can be obtained in a pure state by acidifying with hydrochloric acid, extracting with ether, shaking with aqueous sodium hydrogen sulphite, acidifying the solution so obtained, and finally extracting with ether. W. A. D.

Phenylitaconic Acid and its Isomerides. By RUDOLPH FITTIG and ARTHUR BROOKE (*Annalen*, 1899, 305, 19—41. Compare Fittig and Leoni, Abstr., 1890, 894).—Phenylitaconic acid melts at 192°, evolving water vapour; it crystallises slowly from ether in elongated twinned needles belonging to the asymmetric system, $[a : b : c = 0.82 : 1 : 0.75 ; \ a = 105° 47', \ \beta = 118° 53', \ \gamma = 84° 59']$. The *anhydride* crystallises from chloroform in transparent leaflets belonging to the monosymmetric system, and liquefies at 164—166°, yielding the *anhydride* of phenylcitraconic acid, $C_{11}H_8O_3$; this substance melts at 60—61°, and separates from ether in monosymmetric crystals, $[a : b : c = 0.9498 : 1 : 0.5291 ; \ \beta = 80° 53']$. The anhydride of phenylitaconic acid is regenerated when the anhydride of phenylcitraconic acid is heated at 170°. *Phenylcitraconic acid*, $CH_2Ph \cdot C(COOH){:}CH \cdot COOH$, crystallises from a mixture of ether and petroleum, and melts at 105—108°, losing water; the crystals belong to the asymmetric system, $[a : b : c = 0.5830 : 1 : 0.2467 ; \ a = 122° 25', \ \beta = 103° 15', \ \gamma = 56° 10']$. The *sodium, calcium*, and *silver* salts are anhydrous, whilst the *barium* salt contains $1H_2O$. When boiled with water, phenylcitraconic acid yields about 33 per cent. of phenylitaconic acid.

Phenylmesaconic acid, $CH_2Ph \cdot C(COOH){:}CH \cdot COOH$, separates in leaflets when a small quantity of a dilute solution of bromine in chloroform is added to phenylcitraconic acid exposed to sunlight; it crystallises from boiling water in flattened needles, and melts at 212°. The *calcium* salt contains $2\frac{1}{2}H_2O$, and the *barium* salt $2H_2O$, the *silver* salt being anhydrous.

Phenylaticonic acid, $C_{11}H_{10}O_4$, prepared by the action of boiling aqueous caustic soda on phenylitaconic acid, melts at 149—151°; the crystals from ether are monosymmetric, $[a : b : c = 1.0333 : 1 : 1.0482 ; \ \beta = 60° 55']$. The *calcium* and *barium* salts contain $2H_2O$, and the *silver* salt remains unchanged in weight and appearance at 100°. The *anhydride* crystallises from chloroform in needles, and melts at 138—140°; boiling water converts it into the acid. Phenylitaconic acid is regenerated from phenylaticonic acid by the action of a small

quantity of bromine under the influence of sunlight; the same effect
is produced by a boiling 10 per cent. solution of caustic soda during
20 hours.

The quantitative effects of treating these four acids with a boiling
solution of caustic soda are summarised in tabular form. Benzyl-
succinic acid is obtained on reducing the four isomerides with sodium
amalgam.   M. O. F.

**Action of the Bis-diazochlorides of Benzidine, Ortho-
tolidine, and Orthodianisidine on Acetylacetone.** By G.
FAVREL (*Compt. rend.*, 1899, **128**, 318—319).—*Diphenyldihydrazone-
acetylacetone*, $C_{12}H_8(NH \cdot N \vcentcolon CAc_2)_2$, prepared by adding acetylacetone
to an ice cold solution of tetrazodiphenyl chloride and subsequently
saturating with aqueous caustic soda, sodium carbonate, or, best, with
sodium acetate, is insoluble in the usual solvents, but crystallises
from nitrobenzene or aniline in beautiful, red needles and melts at
258—260°; it is insoluble in aqueous alkalis, but yields, with sodium
ethoxide, a *sodium* derivative which is easily decomposed by water and
does not react with methylic iodide or benzoic chloride. Attempts to
prepare the more complex hydrazones by acting on diphenyldihydr-
azoneacetylacetone with phenylhydrazine were unsuccessful.

Diorthotolyldihydrazoneacetylacetone, $C_{12}H_6Me_2(NH \cdot N \vcentcolon CAc_2)_2$, pre-
pared from tetrazo-orthoditolyl chloride, forms red needles melting at
250—252°, and *diorthanisyldihydrazoneacetylacetone*,

$$C_{12}H_6(OMe)_2(NH \cdot N \vcentcolon CAc_2)_2,$$
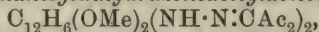
crystallises similarly and melts at 234—235°.   W. A. D.

Orthodiamidodibenzyl. By JOHANNES THIELE and OTTO HOLZ-
INGER (*Annalen*, 1899, **305**, 96—102. Compare Thiele and Dimroth,
Abstr., 1895, i, 534).—Although orthodiamidostilbene, when heated
with the dihydrochloride, yields dihydroindole and aniline (*loc. cit.*),
the corresponding derivative of dibenzyl undergoes the normal change,
yielding orthoimidodibenzyl by elimination of ammonia from two
molecules.

Orthodiamidodibenzyl, $C_2H_4(C_6H_4 \cdot NH_2)_2$, prepared by reducing
orthodiamidostilbene, dissolved in amylic alcohol, with sodium, crystal-
lises from dilute alcohol in small, white needles melting at 68°. The
dihydrochloride crystallises in colourless needles containing $2H_2O$, and
does not melt below 270°, whilst the picrate forms yellow needles which
melt and decompose at 225—230°; the *diacetyl* and *dibenzoyl*
derivatives melt at 249—250° and 255° respectively.

Orthodihydroxydibenzyl, $C_2H_4(C_6H_4 \cdot OH)_2$, obtained from the fore-
foregoing base by decomposing the diazo-compound with water,
crystallises from water and melts at 115°.

Orthodichlorodibenzyl, $C_2H_4(C_6H_4Cl)_2$, crystallises from alcohol in
colourless, lustrous leaflets, and melts at 65°.

Orthoimidodibenzyl, $C_6H_4 \!\!<\!\!{}^{CH_2 \cdot CH_2}_{NH}\!\!>\!\! C_6H_4$, produced on heating
orthodiamidodibenzyl with the anhydrous hydrochloride at 265—275°
during 26—30 hours, melts at 110°, and crystallises from petroleum in
prisms belonging to the monoclinic system [$a:b:c = 1.4308 : 1 : 1.0373$;
$\beta = 91° 52'$]. The substance is volatile in steam, and when dissolved

in concentrated sulphuric acid yields a deep blue coloration with a small quantity of nitric acid. The *nitroso*-derivative crystallises from ether in small, yellow needles, and melts at 120°.

M. O. F.

Triphenylvinylic Alcohol or Triphenylethanone. By HEINRICH BILTZ (*Ber.*, 1899, **32**, 650—658).—The substance, $C_{20}H_{16}O$, prepared by the author from chloral and benzene in presence of aluminium chloride (Abstr., 1893, i, 718), and by Saint-Pierre (*Bull. Soc. Chim.*, 1891, [iii], **5**, 292), Klingemann (Abstr., 1893, i, 590), and Delacre (Abstr., 1896, i, 485), by other methods, may have the formula $CPh_2:CPh\cdot OH$ or $CHPh_2\cdot COPh$. The author prefers the enolic formula, since the substance gives an acetyl (Biltz, Abstr., 1897, i, 533) and a benzoyl derivative, although, like triphenylcarbinol, it does not interact with phenylcarbimide. There is no evidence for the ketonic formula, since the substance does not form an oxime or a phenylhydrazone (Delacre, Biltz), and does not interact with hydrazine or aniline. The presence of a double bond is indicated by the formation of an alcoholate, $OEt\cdot CPh_2\cdot CHPh\cdot OH$, which, when oxidised, yields ethylphenylbenzoin. The dibromide could not be isolated, since it immediately loses hydrogen bromide, and gives the compound $CPh_2Br\cdot COPh$.

Triphenylvinylic benzoate, $CPh_2:CPh\cdot OBz$, crystallises from alcohol in prisms, and melts at 153°; it is readily hydrolysed by alcoholic potash, but is stable towards acids.

The ketonic formula is rendered the less probable by the fact that the closely related phenylbenzoin, $OH\cdot CPh_2\cdot COPh$, readily yields ketonic derivatives. This substance, best prepared by the oxidation of triphenylvinylic alcohol, crystallises from dilute alcohol or from a mixture of chloroform and petroleum, and melts at 84—85°; it is readily reduced to triphenylvinylic alcohol by stannous chloride. *Phenylbenzoinhydrazone*, $OH\cdot CPh_2\cdot CPh:N\cdot NH_2$, crystallises from alcohol in colourless needles, and melts at 167—168°. *Phenylbenzoinmetanitrobenzylidenazine*, $OH\cdot CPh_2\cdot CPh:N\cdot N:CH\cdot C_6H_4\cdot NO_2$, prepared by the action of metanitrobenzaldehyde on the hydrazine, crystallises from alcohol in yellow, transparent needles, and melts at 123°.

The author applies Drude's method for determining the absorption of electric waves, in order to confirm the presence of the hydroxyl-group in the substance (Abstr., 1897, ii, 537), and shows that, whilst the related non-hydroxylic compounds do not absorb these waves, triphenylvinylic alcohol and other hydroxylic compounds exhibit absorption in the liquid, but not in the solid state; triphenylcarbinol and ethylphenylbenzoin, $OH\cdot CPh_2\cdot CO\cdot Ph$, are quoted as exceptions.

T. M. L.

Malachite-green-orthosulphonic Acid. By SUAIS (*Bull. Soc. Chim.*, 1898, [iii], **19**, 25—27).—The sulpho-leuco-bases formed by the interaction of benzhydrols with metasulphanilic acid (compare this vol., i, 58), have the general structure

$$NH_2\cdot C_6H_3(SO_3H)\cdot CH:A_2 \ [NH_2:SO_3H:CH = 1:3:4],$$
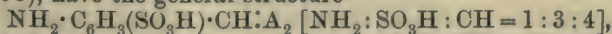
where A denotes a radicle of the type $\cdot C_6H_4\cdot NR_2$. The leuco-base

derived from tetramethyldiamidobenzhydrol (*loc. cit.*) would thus be malachite-green-orthosulphonic acid, $SO_3H \cdot C_6H_4 \cdot C(C_6H_4 \cdot NMe_2)_2$, probably identical with the substance obtained by Sandmeyer by acting on benzaldehydeorthosulphonic acid with dimethylaniline.

W. A. D.

Tetrahydropyrone Compounds. II. By PAVEL IW. PETRENKO-KRITSCHENKO (*Ber.*, 1899, **32**, 809—812).—Not only does hydrochloric acid convert hydropyrones into unsaturated ketones (Abstr., 1898, i, 529), but other mineral acids possess the same property, and it is only necessary to add a few drops of a mineral acid to an alcoholic solution of a hydropyrone, and boil, to bring about its complete conversion into the unsaturated ketone; the following derivatives of hydropyrone also undergo the same reaction.

Orthodimethoxydiphenyltetrahydropyronedicarboxylic acid (*loc. cit.*) melts at 140° when slowly, and at 170° when rapidly, heated, carbonic anhydride being evolved in each case. Its salts are very unstable, and when warmed in aqueous solution, decompose, forming *o*-dimethoxydiphenyltetrahydropyrone (m. p. 171°), which is most conveniently obtained from the acid by adding excess of ammonia and evaporating to dryness.

o-Diethoxydiphenyltetrahydropyronedicarboxylic acid is formed from acetonedicarboxylic acid and orthethoxybenzaldehyde; when quickly heated, it melts at 170°, otherwise at 140°, and when evaporated to dryness with excess of ammonia, gives *o-diethoxydiphenyltetrahydropyrone*, $CO\!<\!\!\begin{array}{c}CH_2(C_6H_4 \cdot OEt)\cdot CH\\CH_2(C_6H_4 \cdot OEt)\cdot CH\end{array}\!\!>\!O$, which separates from alcohol in white crystals melting at 126°, and is completely converted into the unsaturated *ketone*, $CO(CH\!:\!CH \cdot C_6H_4 \cdot OEt)_2$, on boiling its alcoholic solution, containing a trace of hydrochloric acid. This ketone forms yellow crystals, melts at 88°, and dissolves easily in alcohol and ether, but is insoluble in water.

J. F. T.

Structure of Terpenes and Allied Compounds. By ST. TOL-LOCZKO (*Chem. Centr.*, 1898, i, 105; from *J. russ. chem. Ges.*, **29**, 39—63).—In continuation of Wagner's work (*J. russ. chem. Ges.*, **26**, 327; **28**, 56, 484), the author has obtained a hydrocarbon, $C_{20}H_{36}$, by the action of sulphuric acid on menthol; it is a colourless, odourless, viscous liquid, which decolorises potassium permanganate with difficulty, and evolves hydrogen bromide when treated with bromine; it boils at 190—191° under 20 mm. pressure, has a sp. gr. of 0·8814 at 20°/4°, 0·8801 at 22°/4°, 0·8944 at 0°/4°, and a refraction coefficient (Pulfrich's refractometer, $t = 22°$) n_D 1·4841. By the action of sulphuric acid on borneol, the following products are obtained, (1) isocymenesulphonic acid, a liquid which boils at 162—168° and does not decolorise bromine, and (2) a fraction of higher boiling point which distils with difficulty even in a vacuum.

E. W. W.

Oil of Basil. By JUSTIN DUPONT and JACQUES GUERLAIN (*Bull. Soc. Chim.*, 1898, [iii], **19**, 151—154) —A sample of oil of basil obtained

from the island of Réunion has a rotatory power of $[\alpha]_D - 12$, and was proved to consist largely of estragole (paramethoxyallylbenzene); linalool could not be detected. These results have been confirmed by Bertram and Walbaum (Abstr., 1897, i, 625), who have also examined the German oil, and from their analyses, together with the results of the authors' examination of the French oil (Abstr., 1897, i, 429), it appears that specimens obtained from plants cultivated in Europe agree among themselves, but differ greatly in character from the oil from the island of Réunion. N. L.

Ethereal Oil of Jasmine Flowers. II. By ALBERT HESSE and FRIEDRICH MÜLLER (*Ber.*, 1899, **32**, 765—779. Compare this vol., i, 377).—For the estimation of benzylic alcohol and acetate, linalool and linalylic acetate, their different behaviour towards potassium permanganate is made use of. Benzylic acetate is not attacked in neutral or slightly acid solution, and can be determined in the usual way from the weight of the ethereal salt present in the neutral residue after oxidation; benzylic alcohol is converted quantitatively into benzoic acid, and can be estimated as such, whilst linalool and other terpene-alcohols are oxidised to carbonic and acetic acids, and do not give any solid acid; linalylic acetate and other terpene ethereal salts are oxidised in the same way as the alcohols, and can be estimated from the difference in the weight of ethereal salt present before and after oxidation.

The salts present in jasmine-oil have already been shown to be acetates. Benzylic acetate is readily obtained in a pure state, with the normal composition, boiling point, and density, by oxidation with potassium permanganate, and forms 65 per cent. of the oil. Linalylic acetate and other salts of the terpene series form about 7·5 per cent. of the whole, when determined as the difference between the total quantity of ethereal salts and the weight of benzylic acetate. The benzylic alcohol, determined as benzoic acid after oxidation, amounts to 6 per cent. of the whole. The presence of linalool is somewhat difficult to prove directly; on hydrolysing the oil, the neutral residue gives an inactive fraction of high boiling point, consisting chiefly of benzylic alcohol, and a dextrorotatory fraction of low boiling point, which smells strongly of linalool; a considerable part distils near the boiling point of linalool, but the high density and the formation of benzoic acid on oxidation show that benzylic alcohol is also present, and the difference of boiling point is too small to allow of a complete separation. By the action of formic acid on a fraction of low boiling point, a lævorotatory product was obtained which smelt of terpineol, but the lævo-terpineol which is produced from dextro-linalool by this method was not isolated. Similarly, on oxidation with chromic acid, a dextrorotatory product was obtained which smelt of citral, but the latter was not isolated. The quantity of linalool is estimated at 16 per cent., with 5·5 per cent. of other scents. T. M. L.

French Essence of Peppermint. By EUGÈNE CHARABOT (*Bull. Soc. Chim.*, 1898, [iii], **19**, 117—120).—The following results were obtained from four specimens of French essence of peppermint :—

	1 1895.	2 1896.	3 1896. Rectified.	4 1896.
Sp. gr. at 18°	0·921	0·918	0·918	0·918
Rotatory power at 18°	− 6°38′	− 5°54′	− 7°6′	− 6°40′
Ethereal salts	9·5	10·0	9·8	7·1
Free menthol	39·4	35·7	37·8	38·7
Total menthol	46·0	43·7	45·5	44·3
Menthone	9·0	8·8	9·6	8·9

The ethereal salts were proved to include menthylic acetate and valerate. The French essence differs from the Japanese, American, and English varieties in having a slightly higher density, and a considerably lower rotatory power.

[With EBRAY.]—A peculiar modification of the inflorescence, to which the peppermint plant is subject, was found to be due to the punctures of an insect. The essential oil obtained from such plants has a very coarse odour, and differs considerably in composition from the normal product, as is shown by the following analysis: Sp. gr. 0·924 at 18°; rotatory power, + 7°; ethereal salts, 8·2; total menthol, 41·0; menthone, 3·0.   N. L.

Essential Oil of Portugal (Sweet Orange). By JULIAN FLATAU and H. LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], 19, 361—363).—From 500 grams of oil of Portugal, by agitation with saturated sodium hydrogen sulphite solution and decomposition of the precipitate thus obtained with aqueous potash, the authors isolated about 1 gram of a mixture of aldehydic compounds, which included traces of citronellal and 6—7 decigrams of a new *aldehyde* having an odour of oranges. A similar quantity of the oil, when distilled at the ordinary pressure, yielded about 95 per cent. of limonene boiling at 177—179°, whilst from the residue, by successive treatment with alcoholic potash and hydrochloric acid, about 6 grams of an oily, unsaturated *acid* was obtained; this readily absorbs 2 mols. of bromine, with the production of a yellow additive *product* which melts at 94—96°. The *silver* salt is a yellow powder, melting at 138—140°, which decomposes on exposure to light; the *barium* salt is a yellowish powder. The analyses of these compounds indicate for the acid a C_{21}-formula with two ethylenic linkings. The *ethylic* salt, in which form the acid exists in the oil, is best obtained by adding alcohol to the residue left after distillation of the limonene, when it is precipitated in the form of a yellow powder melting at 64—65° and having an odour of oranges; it readily absorbs bromine, with the formation of a pale yellow additive *product* which melts at 56—57°.   N. L.

Essential Oil of Mandarins. By JULIAN FLATAU and H. LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], 19, 364).—A specimen of this oil was found to contain 98 per cent. of limonene, identical with that found in oil of Portugal (see preceding abstract), about 1 per cent. of the ethereal salt also found in that oil, and a trace of citral.   N. L.

Camphor and its Derivatives. By G. BLANC (*Bull. Soc. Chim.*, 1898, [iii], 19, 350—361).—Assuming the validity of the formula

$$\begin{array}{l}\text{CH}_2\!\cdot\!\text{CMe}_2\!\cdot\!\text{CMe}\!\cdot\!\text{COOH} \\ \text{CH}_2 \!\!-\!\!-\!\!-\!\text{CH}\!\cdot\!\text{COOH}\end{array}$$ for camphoric acid, formulæ are deduced for camphor and many of its derivatives. [These formulæ are discussed in a more recent paper by Perkin (Trans., 1898, **73**, 818).]

It is pointed out that the formulæ so obtained for a- and β-campholenic acids, $\begin{array}{l}\text{CH}_2\!\cdot\!\text{CMe}_2\!\cdot\!\text{CHMe} \\ \text{CH}\!\!=\!\!=\!\!=\!\!\text{C}\!\cdot\!\text{CH}_2\!\cdot\!\text{COOH}\end{array}$ and $\begin{array}{l}\text{CH}_2\!\cdot\!\text{CMe}_2\!\cdot\!\text{CMe} \\ \text{CH}_2\!\!-\!\!-\!\!-\!\text{C}\!\cdot\!\text{CH}_2\!\cdot\!\text{COOH}\end{array}$' do not explain the formation of isoketocamphoric and isocamphoronic acids from the former, and of dimethylhexanonoic and dimethylglutaric acids from the latter, so well as those suggested by Tiemann, although these are based on what is considered by the author to be an incorrect formula for camphor. Experiments are being carried out with the object of clearing up this point. N. L.

Camphoric Acid. By G. BLANC (*Bull. Soc. Chim.*, 1898, [iii], **19**, 277—285).—The question of the constitution of camphoric acid is closely connected with that of isolauronolic acid, which is derived from it by the elimination of a carbonyl group and a molecule of water; the author has therefore studied the behaviour of this acid on oxidation. When treated with potassium permanganate and dilute sulphuric acid in the cold, isolauronolic acid is converted into an acid, crystallising in long needles melting at 132° and boiling at 270° under 17 mm. pressure, which is identical with the isolauronic acid of Königs and Meyer, the constitution of which is unknown. If the oxidation takes place at a higher temperature, an oily acid is obtained which is very soluble in water and boils at 260° under 17 mm. pressure; the study of this compound is not yet completed. When heated at 100° with nitric acid of sp. gr. 1·2, isolauronolic acid yields almost exclusively aa-dimethylglutaric acid, which was identified by its conversion into the anhydride, anilide, and phenylimide. [Compare Perkin, Trans., 1898, **73**, 842.] N. L.

Constitution of Camphoric Acid. By G. BLANC (*Bull. Soc. Chim.*, 1898, [iii], **19**, 285—294).—The author examines critically the results obtained by Tiemann, Bredt, Haller, Auwers, Oddo and Manuelli, Balbiano, and Perkin and Thorpe, and discusses their bearing on the question of the constitution of camphoric acid in the light of his own experiments (see preceding abstract). It is urged against Tiemann's formula that it does not account for (1) the profound difference which exists between the two carboxyl groups of camphoric acid, (2) the formation of camphoronic acid by oxidation of camphoric acid, (3) the difference between lauronolic and isolauronolic acids, (4) the formation of aa-dimethylglutaric acid by the oxidation of isolauronolic acid, and (5) the optical inactivity of isolauronolic acid. Bredt's formula accords better with the facts, but is inconsistent with the inactivity of isolauronolic acid, and its conversion into aa-dimethylglutaric acid. Bouveault's formula, on the other hand, explains satisfactorily all the facts known at present. [Compare Perkin, Trans., 1898, 806, *et. seq.*; as to 'Bouveault's formula,' see footnote, *ibid.*, 818.] N. L.

Molecular Transformations Effected by Hydriodic Acid at High Temperatures. By G. BLANC (*Bull. Soc. Chim.*, 1898, [iii], 214—218).—The author points out that the results obtained by reducing compounds of the camphor series with hydriodic acid at a high temperature cannot be considered of any value in discussing their structure, owing to the possibility of molecular change occurring; in support of this contention, the results obtained by Markownikoff in the case of cyclic compounds (Abstr., 1897, i, 401) are cited.

When the acid, $C_{15}H_{20}O_2$, obtained by Bürcker by acting on camphoric anhydride with benzene in presence of aluminium chloride (Abstr. 1891, 324), is heated (10 grams) with concentrated hydriodic acid of sp. gr. 2·0 (20 c.c.) during successive periods of 5 hours each at the temperatures 100°, 150°, 200°, and 210—220°, a large quantity of naphthalene is formed; a considerable proportion of a liquid boiling at 225—270° is also obtained. This result cannot be explained in a simple manner if the acid has the constitution $CHPr{<}{>}CPh{\cdot}OH$ originally assigned to it (Abstr., 1896, i, 179). W. A. D.

Action of Ethylic Oxalate on Camphor. IV. By JOHN BISHOP TINGLE and ALFRED TINGLE (*Amer. Chem. J.*, 1899, **21**, 238—261. Compare Abstr., 1897, i, 484; 1898, i, 443, and Trans., 1890, 652).— Improvements have been made in the preparation of camphoroxalic acid by hydrolysing the mixture of borneol, camphor, and ethylic camphoroxalate together in one operation.

Phenylcamphorformeneamine, $\begin{matrix} CO{-}\\ |\\ C_8H_{14} \end{matrix}{>}C{:}CH{\cdot}NHPh$, is obtained when camphoroxalic acid and aniline, in molecular proportion, are heated at 130° for 30 minutes. It crystallises in colourless, rhombic plates, or occasionally in hair-like needles exceeding an inch in length, melts at 166°, and dissolves readily in alcohol, benzene, or ethylic acetate, but is only sparingly soluble in light petroleum. In alcoholic solution, it gives no coloration with ferric chloride, and when treated with bromine yields a product melting at about 216°. It is not decomposed by boiling with concentrated aqueous sodium hydroxide. The *platinochloride*, $(C_{17}H_2NO)_2,H_2PtCl_6$, crystallises in dark orange coloured needles, and is insoluble in water.

Aniline phenylcamphoformeneaminecarboxylate,
$$C_{17}H_{20}NO{\cdot}COO{\cdot}NH_3Ph,$$
is formed when solutions of camphoroxalic acid (1 mol.) and aniline (2 mols.) in the smallest possible quantities of warm benzene, are mixed and gently heated on the water-bath; the crystals which separate on cooling are recrystallised from a mixture of benzene and light petroleum. It is extremely unstable in presence of even traces of acid vapours. The *acid*, $\begin{matrix} CO{-}\\ |\\ C_8H_{14} \end{matrix}{>}C{:}C(NHPh){\cdot}COOH$, is obtained when the aniline salt is triturated with dilute sulphuric or hydrochloric acid; it is also formed by the action of aniline on sodium camphoroxalate. It crystallises from a mixture of benzene and light petroleum in bright yellow needles, melting and decomposing at 174° when quickly heated, and, when heated above its melting point or at

140° in the presence of ethylaniline, yields carbonic anhydride and phenylcamphoformeneamine. It dissolves in sodium carbonate or hydroxide solution, but prolonged boiling with the latter gives aniline and camphoroxalic acid. The *anilide*, $C_{17}H_{20}NO \cdot CONHPh$, formed when ethylic camphoroxalate is heated with an excess of aniline at 130° for 3 hours, crystallises from a mixture of benzene and light petroleum in colourless needles and melts at 193°.

When camphoroxalic acid is boiled with benzoic chloride and the product recrystallised from benzene and light petroleum, a substance, $C_{22}H_{30}O_4$, melting at 190—191° is obtained, for which the formula

$$\begin{matrix} CH_{14} \\ | \\ CO \end{matrix} \!\!> CH \cdot C \underset{O}{\overset{O}{<\!\!\diamond\!\!>}} C \cdot CH <\!\! \begin{matrix} C_8H_{14} \\ | \\ CO \end{matrix}, \text{ is suggested.}$$
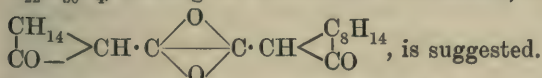
Ethylic camphoroxalate phenylhydrazide, on oxidation with an ethereal solution of hydrogen peroxide, forms two products, of which one crystallises in red needles melting at 210°, and the other melts at 108—109°.

Sodium camphoroxalate, even to the extent of 0·241 gram per kilo. of body weight, has practically no physiological effect. J. J. S.

Sulphonic Derivatives of Camphor. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1898, [iii], **19**, 120—128).—Sulphuric acid alone has little action on camphor at the ordinary temperature, but if coarsely powdered camphor (1 mol.) is added to a well-cooled mixture of acetic anhydride (2 mols.) and sulphuric acid (1 mol.), a liquid product is obtained from which a *camphorsulphonic acid* slowly crystallises, whilst an amorphous isomeric acid may be isolated from the mother liquor.

The crystalline acid, which is shown by analysis and by cryoscopic molecular weight determinations to have the composition $C_{10}H_{15}O \cdot SO_3H$, crystallises from acetic acid in large, doubly-refracting, very hygroscopic prisms, which melt and decompose at 193°, and are very soluble in water, slightly so in cold acetic acid, but almost insoluble in ether. The aqueous solution has a rotatory power $[\alpha]_D = +21°$, and gives no precipitate with barium chloride, even after boiling with excess of potash or nitric acid. The *ammonium* salt crystallises in small, brilliant prisms, very soluble in water; the *barium* salt forms soluble crystalline crusts. The *normal quinine* salt crystallises in small prisms which are very soluble in water, the solution exhibiting a magnificent blue fluorescence; the *basic quinine* salt is much less soluble, melts in boiling water, and crystallises in long needles. *Camphorsulphonic chloride*, $C_{10}H_{15}O \cdot SO_2Cl$, obtained by the action of phosphorus pentachloride on camphorsulphonic acid, crystallises in doubly-refracting plates melting at 67—68°, and is insoluble in water, slightly soluble in light petroleum, readily soluble in ether; it is very slowly acted on by cold, and rather more rapidly by warm water. The *amide*, $C_{10}H_{15}O \cdot SO_2 \cdot NH_2$, exists in two distinct modifications, crystallising respectively in plates melting at 220° and in small prisms melting at 125—126°; the *anilide*, $C_{10}H_{15}O \cdot SO_2 \cdot NHPh$, prepared by heating the chloride with aniline at 100°, crystallises from alcohol in large, doubly refracting prisms which melt at 119° and are

insoluble in water, soluble in alcohol and ether. *Phenylic camphorsulphonate*, $C_{10}H_{15}O \cdot SO_3Ph$, obtained by the action of camphorsulphonic chloride on alcoholic sodium phenoxide, is a thick, oily liquid, insoluble in water. The *oxime*, $SO_3H \cdot C_{10}H_5 \colon NOH$, prepared by Beckmann's general method, crystallises in large prisms which decompose at 177—178°, and are soluble in water, but less soluble in boiling alcohol. The *phenylhydrazone*, $OH \cdot SO_2 \cdot C_{10}H_{15} \colon N_2HPh$, crystallises in small, brilliant plates which melt and decompose at 235°, and are insoluble in water, but very soluble in aqueous potash; it reduces Fehling's solution slowly in the cold, and rapidly on warming. The action of excess of phenylhydrazine on camphorsulphonic chloride in ethereal solution leads to the formation of a *compound*, possibly $NHPh \cdot NH \cdot SO_2 \cdot C_{10}H_{15} \colon N_2HPh$, which crystallises in slender needles melting at 149—151°. It is insoluble in water, is decomposed with effervescence by warm aqueous potash, and rapidly reduces Fehling's solution in the cold.

The amorphous camphorsulphonic acid which is formed along with, although in smaller quantity than, the isomeric crystalline acid, was obtained only as a yellowish, syrupy mass, extremely soluble in water. The *barium* salt is a yellowish, amorphous, pulverulent substance, whilst the *ammonium* salt was obtained as an amorphous, gummy mass sometimes showing signs of crystallisation on keeping. The *chloride*, which could not be obtained in a pure state, is an insoluble oil. Unsuccessful attempts to prepare a phenylhydrazone seem to show that the amorphous acid does not contain the carbonyl group.

These acids are, therefore, not identical with Kipping and Pope's camphorsulphonic acid (Trans., 1893, **63**, 573).   N. L.

Stick-lac. By ALEXANDER TSCHIRCH and A. FARNER (*Arch. Pharm.*, 1899, **237**, 35—48).—The wax was removed from the coarsely powdered lac by extraction with pure light petroleum in a reflux apparatus (compare Benedikt and Ulzer, Abstr., 1888, 1309; Gascard, *J. Chim. Pharm.*, 1893, 365). The residue was extracted with warm water, the aqueous extract concentrated and precipitated with lead acetate; by decomposing the precipitate with sulphuric acid, the crude colouring matter was obtained (compare R. E. Schmidt, Abstr., 1887, 734). Finally, the purified resin was obtained by treating the residual lac with an equal weight of hot alcohol, filtering into 4—5 times the quantity of water, and adding a few drops of dilute hydrochloric acid. The residue insoluble in the alcohol consisted of woody matter, carapaces of insects, colouring matter, &c.

The resin formed a bulky, amorphous, light brown powder. It was dissolved in an equal weight of alcohol, and the solution mixed cautiously with 8—10 times the weight of ether, and then shaken vigorously. The precipitate which formed was washed with ether, dissolved in alcohol, and precipitated by pouring the solution into a large quantity of water and adding a few drops of hydrochloric acid; it forms a white, amorphous powder devoid of acid properties. In order to hydrolyse it, it was dissolved in 10 per cent. caustic potash, and the solution boiled for several hours while a current of steam

was passed through it; the hot solution was then acidified with sulphuric acid, when a crystalline precipitate formed on cooling; this was filtered off and the solution extracted with ether, the process being repeated until only a negligible amount of substance was extracted. The united crystalline precipitates and residues obtained on evaporating the ethereal extracts were then heated with water and excess of magnesium carbonate, the solution was treated with animal charcoal, and the magnesium salt crystallised and decomposed with hydrochloric acid; the acid which separated was recrystallised several times from alcohol and water. It is named *aleuritic acid*; it melts at 101·5°, and has the composition $C_{13}H_{26}O_4$; it is a monobasic acid, but forms *magnesium*, *lead*, and *barium* salts of the type $(C_{12}H_{25}O_2 \cdot COO)_2M'', C_{12}H_{25}O_2 \cdot COOH$; probably it is a dihydroxyundecoic acid. The other product of the hydrolysis of the resin could only be obtained as a sticky substance; it appears to be a *resinotannol* (Abstr., 1894, ii, 361), but was probably mixed with fatty acids. The resin insoluble in ether may thus be regarded as the resinotannol salt of aleuritic acid, the two hydroxyl groups of the latter having at the same time condensed with fatty acids. Stick-lac thus resembles amber in the fact that its resin contains fatty acids; all other resins hitherto examined contain only aromatic acids.

The ethereal solution, containing part of the original resin still dissolved, was agitated gently with successive quantities of aqueous 1 per cent. sodium carbonate solution, 20—25 litres being used for 100 grams of the resin; it was impossible to shake vigorously, as the liquids then formed an emulsion. The remaining ethereal solution contains a white substance of the nature of a *resin*; the amount of this equals about $1\frac{1}{2}$ per cent. of the crude product. The soda solution was precipitated with aqueous lead acetate; the precipitate was suspended in alcohol, warmed, and decomposed with sulphuric acid, and the solution treated with animal charcoal and precipitated with alcoholic lead acetate; a violet lake was precipitated, and the filtrate, when treated with sulphuric acid, yielded a sticky substance with a strong odour of shellac, and apparently consisting of fatty acids; this substance forms the bulk of the resin soluble in ether. The violet lake was decomposed with alcohol and sulphuric acid, and the solution poured into water to precipitate the colouring matter, from which a substance, named *erythrolaccin*, was eventually isolated. It forms about 1 per cent. of the purified resin, is yellow to red in colour; when heated, it decomposes, but sublimes in part; with strong sulphuric acid, it forms a bluish-violet solution, which gives three absorption bands between $\lambda = 0·640$—$0·680$, $0·540$—$0·560$, and $0·500$—0525μ; it has the composition $C_{15}H_{10}O_5 + H_2O$, and appears to be a hydroxymethylanthraquinone, most nearly resembling methylquinalizarin of those at present known.

Stick-lac contains wax 6, colouring-matter 6·5, purified resin 74·5 (of which 65 per cent. is insoluble, and the remainder soluble in ether), residue 9·5 and water, &c., 3·5 per cent.

Bleached lac was also examined; like the unbleached material, it contains aleuritic acid, but no wax, and all its constituents contain

considerable quantities of chlorine; moreover, it is not entirely soluble in alcohol, a substance resembling "Lackstoff" being left undissolved. The bleaching of the lac is due to the destruction or alteration of the erythrolaccin.   C. F. B.

Chemical Constituents of Fabiana Imbricata. By HERMANN KUNZ-KRAUSE (*Arch. Pharm.*, 1899, **237**, 1—35).—*Fabriana imbricata* (Ruiz and Pavon), or Pichi-pichi, is a shrub which occurs in dry districts of Chili, between 29° and 37° S. latitude, and from 1000 to 6500 feet above sea level; it is one of the *Solanaceæ*, but in adapting itself to its environment it has acquired some of the external characters of the *Coniferæ*. Of late years, it has been employed in Europe as a drug, and has been investigated chemically, but not in an exhaustive fashion. The material employed in the present investigation consisted of a syrupy "fluid extract" (alcoholic) and a plastic "extr. spissum," in addition to the drug itself.

The powdered leaves were extracted twice with hot water, then exhausted with ether in a Soxhlet apparatus, and finally extracted with alcohol. The aqueous extract contained magnesium phosphate, which was precipitated on adding ammonia; from the filtrate, lead acetate precipitated *fabianaglucotannoid* mixed with a little chrysatropic acid; after these were removed, potassium mercuri-iodide precipitated choline (no other alkaloid could be detected), and on removing this and adding common salt, a soft, resinous substance was thrown down, whilst from the residual solution, ether extracted a liquid that appeared to contain formic acid, but consisted mainly of the same *resin*; this resin is apparently the parent substance of all the compounds obtained; when boiled with dilute sulphuric acid, it yields fabianol, chrysatropic acid, and a *sugar* which reduces Fehling's solution, but is optically inactive, and was not obtained crystallised. The ethereal extract yielded *fabianol* when distilled with steam; by adding ammonia to the residue and diluting with water, a precipitate of *fabianaresen* was obtained, and from the filtrate from this, after acidification with sulphuric acid, chloroform extracted chrysatropic acid (4-hydroxy-5-methoxycoumarole, $C_{10}H_8O_4$) melting at 204°. The alcoholic extract contained fabianaglucotannoid, choline, and a trace of substance smelling like vanillin.

The powdered wood was extracted with alcohol and ether successively; the alcoholic extract contained chrysatropic acid and choline; the ethereal extract chrysatropic acid and a substance which formed acraldehyde when heated with "primary" potassium sulphate.

The commercial extracts were freed from alcohol, and extracted with water; the aqueous extract contained chrysatropic acid, choline, fabianaglucotannoid and—after boiling with 1 per cent. sulphuric acid —fabianol; from the residue, fabianol could be distilled over with steam, while fabianaresen was left behind. A somewhat larger yield of fabianol was obtained by dissolving the original extract in caustic soda and distilling with steam; the residue, after acidification, had a distinct odour of butyric acid.

If it is desired to obtain the glucotannoid and resen only, it is best to extract the leaves with chloroform and hot water successively; the

chloroform extract yields fabianaresen, which is washed with cold dilute alcohol and crystallised from boiling alcohol, animal charcoal being employed to effect decolorisation; the aqueous extract, when evaporated, leaves fabianaglucotannoid, which is purified by dissolving it in a little water and precipitating it with alcohol, the process being repeated several times.

Fabianaresen is a white, crystalline substance which melts at about 280° and can be sublimed ; on chemical grounds, the author prefers the formula $C_{54}H_{90}O_6$ for it, although a cryoscopic determination of the melting point is in accordance with the simpler formula, $C_{18}H_{30}O_2$. When it is treated with bromine in ethereal or alcoholic solution, a colourless *bromo*-derivative, $C_{18}H_{28}Br_2O_2$ is formed, which can be obtained crystallised ; when boiled with bromine in acetic acid solution, it yields a yellow product, apparently a mixture of perbromides ; the colourless bromo-derivative may be obtained from this by dissolving it in the minimum quantity of benzene and diluting the solution with 50 per cent. alcohol. Boiling with acetic acid has no effect on fabianaresen, but by heating it with acetic anhydride and sodium acetate at 120°, it can be made in part to yield an *acetyl* derivative, $C_{18}H_{29}AcO_2$, which melts at 234° after softening at 215°. When heated with benzoic anhydride at 150—160°, it yields a *benzoyl* derivative, $C_{18}H_{29}BzO_2$, which melts at 61°. Sodium has little action on fabianaresen in chloroform solution ; hydriodic acid of sp. gr. 1·7 and phosphorus at 250° reduce it to a waxy *substance*, $C_{54}H_{98}O_2$, the formation of which is most simply explained by adopting the triple formula for fabiana-resen. The resen is not affected by boiling with alcoholic potash ; when it is fused with a mixture of potassium and sodium hydroxides, a *product* is obtained which melts at 178—180° after softening at 125°, is acid in character, and in its colour reactions with concentrated sulphuric acid resembles hesperetol (vinylparamethoxycatechol) and vinylcatechol (Abstr., 1894, ii, 328).

Fabianaglucotannoid is a yellow, very hygroscopic substance, which reduces alkaline silver and copper solutions; it softens at 80° and begins to swell up at about 105° ; it exhibits many of the reactions of the tannic acids of maté and coffee. It contains C 42·30 and H 5·65 ; if it is distilled with aqueous potash, the distillate yields iodoform when treated with potash and iodine solution, and the residual substance is no longer hygroscopic; with bromine water, an orange precipitate, apparently of dibromomethoxydihydroxycinnamic acid, is obtained. Possibly the glucotannoid has the constitution

$$C_6H_{11}O_5 \cdot O \cdot C_6H_2(OH)(OMe)CH:CH \cdot COOH,$$
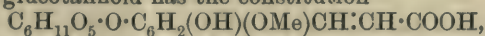
or is an intramolecular anhydride of this ; its yellow *lead* and green *copper* salts have a percentage of metal corresponding with that required for the basic formula $C_{32}H_{36}O_{20}M''_2 + 2H_2O$, and, although insoluble in water, are soluble even in very weak acids and alkalis.   C. F. B.

The **Quinquevalent Asymmetric Nitrogen Atom. III. 1-Hydroxypiperidiniumacetic Acid.** By Edgar Wedekind (*Ber.*, 1899, **32**, 722—728. Compare this vol., i, 357).—Hydroxypiper-idiniumacetic acid, $CH_2 \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} NH(OH) \cdot CH_2 \cdot COOH$, prepared

by the action of chloracetic acid on aqueous piperidine (Kraut), or by hydrolysing ethylic piperidyloacetate (Bischoff and Stefanowski, this vol., i, 229), separates from alcohol in sphenoidal, hemihedric crystals belonging to the rhombic system ; [$a : b : c = 0.9462 : 1 : 0.5887$]. Although both enantiomorphous forms are produced on crystallisation from alcohol (compare Miss Evans, Trans., 1897, **71**, 522), the fractions consist almost exclusively of left-handed crystals ; these are optically inactive, and although capable of supporting a culture of *Penicillium glaucum,* an aqueous solution which has been submitted to the influence of the organism during three weeks remains inactive at the end of this period.

Attempts to substitute alkyl groups for the hydrogen attached to the nitrogen atom in hydroxypiperidiniumacetic acid result in the production of ammonium salts of the corresponding halogen hydrides ; when these are treated with silver oxide, hydroxypiperidiniumacetic acid is regenerated.   M. O. F.

Ammonium Salt of Ethylic 2 : 6-Dihydroxynicotinate. By MAX GUTHZEIT (*Ber.*, 1899, **32**, 779—782).—The compound prepared by Errara by boiling an alcoholic solution of diethylic αγ-dicyano-glutaconate (Abstr., 1898, i, 297), and formulated as the diamide of diethylic dicarboxyglutaconate,

$$COOEt \cdot CH(CO \cdot NH_2) \cdot CH : C(CO \cdot NH_2) \cdot COOEt$$
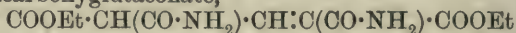
(*ibid.*, 490), is shown to be identical with the ammonium salt of ethylic dihydroxynicotinate [OH : COOEt : COOEt : OH = 2 : 3 : 5 : 6]. The latter is, however, a monobasic acid, the *silver* and *copper* salts being described in addition to the sodium and ammonium salts, and the author, therefore, regards it as being the ketonic form,
$$\begin{array}{c} COOEt \cdot C \cdot CH : C \cdot COOEt \\ OH \cdot C \cdot NH \cdot CO \end{array}$$
, and not a normal pyridine derivative.   T. M. L.
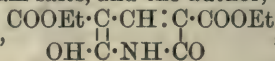
Action of Alkylic Iodides on Indoles. Action of Ethylic Iodide on 2′-Methylindole (Methylketole). By GIUSEPPE PLANCHER (*Gazzetta*, 1898, **28**, ii, 333—373).—Fischer and Steche, and Ciamician and Plancher, have shown that, by ethylating methylketole, three products are obtained having the formulæ $C_{11}H_{13}N$, $C_{13}H_{17}N$, and $C_{15}H_{21}N$. The first of these, to which the name 2′-methyl-1′-ethylindole has been given, the author has identified with 2′-methyl-3′-ethylindole, $C_6H_4\!\!<^{CEt}_{NH}\!\!>CMe$, obtained by Fischer by condensing the phenyl-hydrazone of methyl propyl ketone by means of zinc chloride ; it is a dense, colourless liquid boiling at 192—195° under 50 mm. pressure, and forms a picrate melting at 152—153°.

The second ethylation product, which can also be obtained by the action of ethylic iodide on 2′-methyl-3′-ethylindole, has been formerly regarded as a dihydroquinoline derivative of the constitution $C_6H_4\!\!<^{-CEt_2-}_{NH \cdot CH}\!\!>CH$; the fact that it is stable towards permanganate tends to show that the double linking exists, not between two carbon atoms, but between a carbon and a nitrogen atom, as is the case with the oximes and with benzylideneaniline, and the author finds that the compound is really 2′-methyl-3′ ; 3′-diethylindolenine,

$C_6H_4 <^{CEt_2}_{-N} > CMe$. It is produced from 2′-methyl-3′-ethylindole by the direct addition of ethylic iodide and the splitting off of hydrogen iodide. It forms a sparingly soluble picrate melting at 189—190°, which serves for its separation. When 2′-methyl-3′ : 3′-diethylindolenine is acted on by hot permanganate solution, its 2′-methyl group is oxidised, giving rise to 3′: 3′-diethylindolenyl-2′-carboxylic acid, $C_6H_4 <^{CEt_2}_{-N} > C \cdot COOH$, which melts at 125° with loss of carbonic anhydride and formation of 2′: 2′-diethyindolenine, $C_6H_4 <^{CEt_2}_{-N} > CH$; this compound, like the homologous dimethyl base obtained by Brunner (Abstr., 1896, i, 169 and 625), forms, with methylic iodide, an additive compound, $C_{12}H_{15}N,MeI$, melting with decomposition at 132°. When this methiodide is acted on by potassium hydroxide, its iodine is replaced by hydroxyl, forming 1′-methyl-3′: 3′-diethylindolinol, $C_6H_4 <^{CEt_2}_{NMe} > CH \cdot OH$; this substance, which has a pungent odour, is soluble in ether and melts at 55°; it is a homologue of Brunner's trimethylindolinole, for bromine water oxidises and brominates it, giving the dibromo-derivative of 1′-methyl-3′ : 3′-diethylindolinone, $C_6H_2Br_2 <^{CEt_2}_{NMe} > CO$, which melts at 92—93° and separates from light petroleum in orthorhombic crystals ; $[a : b : c = 0 \cdot 45907 : 1 : 1 \cdot 38622]$.

On treating 2′-methyl-3′-ethylindole with methylic iodide, the compound formerly known as 1′-methyl-4′:4′-diethyldihydroquinoline is obtained; the author's researches show this to be 1′-methyl-3′ : 3′-diethyl-2′-methylenindoline. It is a liquid lighter than water, and boils at 147—150° under 25 mm., and at 257—260° under 753 mm. pressure ; by sodium and alcohol, it is reduced to 1′ : 2′-dimethyl-3′ : 3′-diethylindoline, $C_{14}H_{21}N$, which boils at 154—158° under 25 mm. pressure, and forms a platinochloride, $(C_{14}H_{21}N)_2,H_2PtCl_6$, melting and decomposing above 200°. When treated with phosphorus and hydriodic acid, this reduced base yields 2′-methyl-3′: 3′-diethylindoline, $C_{13}H_{19}N$, which melts at 217° and gives a picrate forming triclinic crystals melting at 138°; $[a : b : c = 1 \cdot 97272 : 1 : 1 \cdot 41341 ; a = 113° 36′, \beta = 111° 30′, \gamma = 63° 18′]$. The same base, $C_{13}H_{19}N$, is obtained on reducing 2′-methyl-3′ : 3′-diethylindolenine.

From 2′-methyl-3′-ethylindole, the analogous 1′:3′ : 3′-triethyl-2′-methylenindoline, $C_6H_4 <^{CEt_2}_{NEt} > C \colon CH_2$, is obtained by substituting ethylic for methylic iodide ; it is the third ethylation product of methylketole. It is a colourless, mobile liquid boiling at 265° under 760 mm. pressure, and reddens on long exposure to the air; its picrate crystallises from absolute alcohol in pale yellow, monoclinic prisms melting at 119—120°; $[a : b : c = 0 \cdot 84090 : 1 : 0 \cdot 63396 ; \beta = 70° 51′]$. This base, and the corresponding methyldiethyl compound described above, are readily oxidised by permanganate solution.

Of similar constitution to these two indoline derivatives is the compound formerly described under the name trimethyldihydroquinoline,

and hence must be $1' : 3' : 3'$-trimethyl-$2'$-methylenindoline; if it is submitted first to reduction, then to demethylation by means of hydriodic acid, and finally to oxidation with permanganate, $1' : 3' : 3'$-trimethylindolenine is obtained, thus:

$$C_6H_4 {<}^{CMe_2}_{NMe}{>} C{:}CH_2 \quad \rightarrow \quad C_6H_4 {<}^{CMe_2}_{NMe}{>} CHMe \quad \rightarrow$$

$$\rightarrow \quad C_6H_4 {<}^{CMe_2}_{\cdot NH\cdot}{>} CHMe \quad \rightarrow \quad C_6H_4 {<}^{CMe_2}_{\underline{\quad}N}{>} CMe.$$
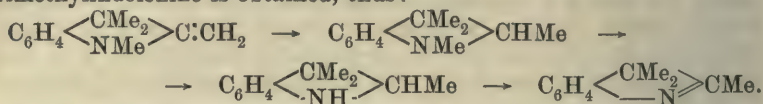
When heated with sodium acetate and acetic anhydride, $2'$-methyl-$3' : 3'$-diethylindolenine yields an acetyl compound derived from its tautomeric form and having the constitution $C_6H_4 {<}^{CEt_2}_{NAc}{>} C{:}CH_2$. On heating in a closed tube with acetic anhydride, this acetyl derivative is converted into an isomeric form, probably of the constitution $C_6H_4 {<}^{CEt_2}_{\underline{\quad}N}{>} C{\cdot}CH_2Ac$; this separates from light petroleum in colourless triclinic crystals melting at 113—$114°$; $[a : b : c = 1{\cdot}080084 : 1 : 0{\cdot}73202$; $a = 83°\ 28'$, $\beta = 102°\ 13'$, $\gamma = 98°\ 54']$. On boiling the latter acetyl compound with dilute hydrochloric acid, it is converted into $2'$-methyl-$3' : 3'$-diethylindolenine.   T. H. P.

Action of Alkylic Iodides on Indoles. $1' : 3'$-Dimethyl-$3'$-ethyl-$2'$-methylenindoline. By GIUSEPPE PLANCHER (*Gazzetta*, 1898, 28, ii, 374—391).—By the action of ethylic iodide on $1' : 2' : 3'$-trimethylindole, Ciamician and Boeris (Abstr., 1897, i, 102) obtained a tertiary base of the composition $C_{13}H_{17}N$, which, according to the author's views, must be $1' : 3'$-dimethyl-$3'$-ethyl-$2'$-methylenindoline, $C_6H_4 {<}^{CMeEt}_{\cdot NMe}{>} C{:}CH_2$, and should also be formed by the interaction of $2'$-methyl-$3'$-ethylindole and methylic iodide; the author has shown that these two reactions give rise to one and the same base. The picrate, $C_{13}H_{17}N, C_6H_2(NO_2)_3{\cdot}OH$, crystallises from alcohol in golden-yellow scales melting at 113—$114°$. The benzoyl derivative, $C_{13}H_{16}NBz$, crystallises from light petroleum in monoclinic prisms melting at 119—$120°$; the crystallographic constants of the benzoyl derivatives of the bases obtained by these two methods are as follows:—(1) From the trimethylindole; $[a : b : c = 0{\cdot}93529 : 1 : 0{\cdot}60169$; $\beta = 89°\ 23']$. (2) From the ethylmethylindole; $[a : b : c = 0{\cdot}93637 : 1 : 0{\cdot}60446$; $\beta = 89°\ 26']$.

On oxidation with alkaline permanganate, this tertiary base gives rise to the $1' : 3'$-dimethyl-$3'$-ethylindolinone, $C_6H_4 {<}^{CMeE}_{NMe-}{>} CO$, as this, on treatment with bromine water, gives the dibromo-derivative, $C_{12}H_{13}NBr_2O$, which is soluble in the ordinary organic solvents, and crystallises from dilute acetic acid in monoclinic needles melting at 121—$122°$; $[a : b : c = 2{\cdot}36199 : 1 : 2{\cdot}97023$; $\beta = 82°\ 39']$.

When heated with zinc chloride, the phenylhydrazone of diethylketone condenses, forming $3'$-methyl-$2'$-ethylindole, $C_6H_4 {<}^{CMe}_{\cdot NH\cdot}{>} CEt$, which crystallises from light petroleum in colourless plates melting at

66°; it forms a picrate crystallising in red needles melting at 150—151°, and a nitroso-derivative which shows Liebermann's colour reaction for nitrosamines.

By the action of methylic iodide on 3'-methyl-2'-ethylindole, 1' : 3'-dimethyl-3'-ethyl-2'-methylenindoline is formed, its identity with the compounds obtained from 1' : 2' : 3'-trimethylindole and from 2'-methyl-3'-ethylindole being established by the crystal measurements of its benzoyl derivative.   T. H. P.

Action of Alkylic Iodides on Indoles. Action of Methylic Iodide on 2'-Phenylindole. By GIUSEPPE PLANCHER (*Gazzetta*, 1898, **28**, ii, 391—403).—When methylic iodide acts on 2'-phenylindole, $C_6H_4{<}^{CH}_{NH}{>}CPh$, a hydriodide of the composition $C_{17}H_{17}N,HI$, is obtained, which crystallises in almost colourless prisms melting with decomposition at 226—227°. It is very soluble in hot methylic or ethylic alcohol, from which it is precipitated by ether or ethylic acetate; it is also slightly soluble in water. Digestion of this hydriodide with solutions of alkalis liberates the base, *3'-phenyl-1' : 3'-dimethyl-2'-methylenindoline*, $C_6H_4{<}^{CMePh}_{-NMe-}{>}C{:}CH_2$, which separates from light petroleum in crystals melting at 104—105° and is readily oxidised by permanganate in either acid or alkaline solution, although no definite products have as yet been isolated. The *platinochloride*, $(C_{17}H_{17}N)_2,H_2PtCl_6$, melts and decomposes at 223—224°. The *acetyl* derivative, $C_6H_4{<}^{CMePh}_{NMe}{>}C{:}CHAc$, separates from ethylic acetate in yellowish, triclinic crystals melting at 142° [$a:b:c = 0.81919:1:0.86421$; $a = 102°\ 6'$, $\beta = 106°\ 58'$, $\gamma = 89°\ 27'$], and the *benzoyl* derivative, $C_{17}H_{16}NBz$, crystallises from ethylic acetate and melts at 141°; both these derivatives are stable towards permanganate.

On reducing the base with tin and hydrochloric acid, it is converted into 3'-phenyl-1' : 2' : 3-trimethylindoline, $C_6H_4{<}^{CMePh}_{-NMe-}{>}CHMe$, which separates as a colourless oil; it gives a hydriodide, $C_{17}H_{19}N,HI$, which forms colourless crystals melting at 227—228°, and dissolves in water or alcohol slightly in the cold, moderately on heating. The reduced base is completely demethylated by heating with phosphorus and hydriodic acid.   T. H. P.

Action of Alkylic Iodides on Indoles. Action of Nitrous Acid on 2'-Methyl-3':3'-diethylindolenine. By GIUSEPPE PLANCHER (*Gazzetta*, 1898, **28**, ii, 405—418).—On treating a cold glacial acetic acid solution of 2'-methyl-3' : 3'-diethylindolenine with a slight excess of aqueous potassium nitrite, *3':3'-diethylindolenine-2'-formoxine*, $C_6H_4{<}^{CEt_2}_{-N}{>}C{\cdot}CH{\cdot}NOH$, is produced; it forms silky needles melting at 169°, and is soluble in alcohol, readily so in boiling benzene, but is only slightly dissolved by light petroleum or by water. It dissolves in dilute caustic alkali with a yellow coloration, and from its solution in concentrated mineral acids or in glacial acetic acid, it is precipitated unchanged by dilution or by neutralisation with

alkali carbonates. In cold alcoholic solution, it is stable towards 2 per cent. aqueous permanganate, but on rendering alkaline it is immediately oxidised. Cryoscopic examination of its solution in phenol shows that its molecular weight corresponds with that required for the formula $C_{13}H_{16}N_2O$. The oxime gives a crystalline benzoyl derivative, and on heating with five times its weight of acetic anhydride, forms an *acetyl* derivative, $C_6H_4{<}^{CEt_2}_{N}{>}C\cdot CH\cdot NOAc$, which crystallises from dilute alcohol in well-defined, transparent laminæ melting at 100°. If the heating with acetic anhydride is continued, 3′: 3′-*diethylindolenine-2′-nitrile*, $C_6H_4{<}^{CEt_2}_{N}{>}C\cdot CN$, is obtained in quantitative yield. It is a colourless, mobile liquid, with a pleasing odour, and boils at 163—164° under 27 mm. pressure. The ordinary organic solvents and water dissolve it, and it is not hydrolysed by acids or by caustic alkalis. When mixed with equivalent quantities of hydroxylamine hydrochloride and sodium carbonate and gently heated, 3′: 3′-*diethylindolenine-2′-formamidoxime*, $C_6H_4{<}^{CEt_2}_{N}{>}C\cdot C{<}^{NOH}_{NH_2}$, is obtained; this melts at 121—122°, and crystallises from alcohol in colourless needles or prisms arranged in rows or crosses. On hydrolysing the nitrile with alcoholic potash, two products are obtained. The first is the corresponding 3′: 3′-diethylindolenine-2′-carboxylic acid, $C_6H_4{<}^{CEt_2}_{N}{>}C\cdot COOH$, which is identical with the acid obtained from 3′: 3′-diethyl-2′-methylindolenine by oxidation with permanganate. The second product is 3′: 3′-diethylindolinone, having the tautomeric formulæ $C_6H_4{<}^{CEt_2}_{N}{>}COH$, and $C_6H_4{<}^{CEt_2}_{NH}{>}CO$; it melts at 157—158°, and forms a dibromo-derivative, $C_{12}H_{13}NOBr_2$, which separates from dilute alcohol in colourless crystals melting at 171°.

The author calls attention to the similarity of the two groups, ·N:CMe· and ·O·CMe·, contained in the indolenines and in acetone respectively, and suggests that the transformations of 3′: 3′-diethyl-2′-methylindolenine into oxime, thence into nitrile, and the hydrolysis of the latter into two different products, are analogous to the corresponding series of changes starting with acetone :

$$COMe\cdot CH_3 \longrightarrow COMe\cdot CH{:}NOH \longrightarrow COMe\cdot CN \underset{\searrow}{\overset{\nearrow}{}} \begin{array}{l} COMe\cdot COOH. \\ Me\cdot COOH \end{array}$$

.   T. H. P.
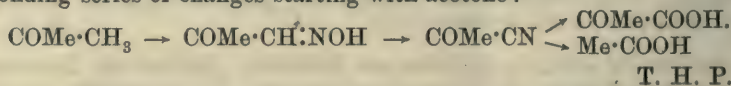
Synthesis of the Bases formed by the Methylation of Indole.

By GIUSEPPE PLANCHER (*Gazzetta*, 1898, **28**, ii, 418—433).—The author has confirmed his views (Abstr., 1898, i, 536) regarding the constitution of 2′: 3′: 3′-trimethylindolenine and 1′: 3′: 3′-trimethyl-2′-methylenindolenine, by preparing them synthetically from the phenylhydrazone of isobutaldehyde by Brunner's method (Abstr., 1896, i, 169 and 625).

When the phenylhydrazone of methyl isopropyl ketone is heated in alcoholic solution with zinc chloride, it is converted into 2′: 3′: 3′-trimethylindolenine, identical in all its properties with the base

obtained by oxidising 2′ : 3′ : 3′-trimethylindoline ; the condensation takes place as follows :—

$$\begin{matrix} CHMe_2 \\ C_6H_5 \cdot NH \cdot N \end{matrix} \!\!>\!\! CMe \quad \rightarrow \quad C_6H_4 \!\!<^{CMe_2}_{\;\;N}\!\!>\!\! CMe.$$

This shows that Brunner's process permits of extension to ketones having a ·CH:-group joined to the carbonyl and that in the case of the phenylhydrazone of a ketone having a ·CH: and a CH_3-group joined to the carbonyl, the hydrogen of the former is expelled in preference to that of the latter. The action of methylic iodide on the above trimethylindolenine and the condensation of the methyl-phenylhydrazone of methyl isopropyl ketone both yield 1′ : 3′ : 3′-tri-methyl-2′-methylenindoline, identical with Fischer's trimethyldihydro-quinoline.

By heating the phenylhydrazone of di-isopropyl ketone in presence of zinc chloride, it condenses to 3′ : 3′-*dimethyl-2′-isopropylindolenine*, $C_6H_4 \!\!<^{CMe_2}_{\;\;N}\!\!>\!\! CPr^\beta$, which crystallises from light petroleum in prisms, melts at 80° and boils at 250—260° ; it is hydrolysed even by dilute acids, is stable towards permanganate, and in benzene has the normal molecular weight. On methylation, it yields 1′ : 3′ : 3′-tri-methyl-2′-isopropylidenindoline, $C_6H_4 \!\!<^{CMe_2}_{NMe}\!\!>\!\! C:CMe_2$, identical with the pentamethyldihydroquinoline obtained by Zatti and Ferratini (Abstr., 1890, 1292), and by Piccinini (this vol., i, 76) ; this forms a hydriodide melting with decomposition at 185°, and an aurichloride which separates from dilute hydrochloric acid in yellow crystals melting at 150°, also with decomposition.   T. H. P.

Constitution of Bases formed by the Action of Alkylic Iodides on Indoles. By GIUSEPPE PLANCHER and D. BETTINELLI (*Real. Accad. Linc.*, 1898, i, 367—372. Compare Abstr., 1898, i, 536). —It has previously been shown that the so-called trimethyldihydro-quinoline has most probably the constitution $C_6H_4 \!\!<^{CMe_2}_{NMe}\!\!>\!\! C:CH_2$, but the formulæ $C_6H_4 \!\!<^{-CMe_2-}_{N(CH_2)}\!\!>\!\! CMe$ and $C_6H_4 \!\!<^{CMe_2 \cdot \, C\, Me}_{\;\;\;N}\!\!\! - \!\!\!>\!\! CH_2$ have also been suggested for this compound. If trimethyldihydro-quinoline is represented either by the second or third formula, tetra-methyldihydroquinoline, having similar properties, must be either $C_6H_4 \!\!<^{-CMe_2-}_{N(CHMe)}\!\!>\!\! CMe$ or $C_6H_4 \!\!<^{CMe_2 \cdot \, C\, Me}_{\;\;\;N}\!\!\! - \!\!\!>\!\! CHMe$, and since tri-methyldihydroquinoline is obtained by the action of methylic iodide on 2′ : 3′ : 3′-trimethylindolenine, $C_6H_4 \!\!<^{CMe_2}_{\;\;N}\!\!>\!\! CMe$, it follows that the base formed by the action of ethylic iodide on the same indolenine would in either case be identical with tetramethyldihydroquinoline. This, however, is found not to be the case, the product of the reaction being the hydriodide of a new base, 3′ : 3′-*dimethyl-1′-ethyl-2′-methyl-eneindoline*, $C_6H_4 \!\!<^{CMe_2}_{NEt}\!\!>\!\! C:CH_2$, which crystallises from alcohol in colourless scales melting at 219°, and from which the base can be

set free with potash. The latter turns red on exposure to air, is lighter than water, almost odourless, and readily soluble in dilute acids; it forms a *picrate*, crystallising in yellowish scales melting at 125°, and a *benzoyl* derivative which crystallises in prisms melting at 140°.   N. L.

4-Nitrocinchonic Acid and 4-Amidocinchonic Acid. By WILHELM KOENIGS and EMIL LOSSOW (*Ber.*, 1899, **32**, 717—720).—4-*Nitroquinoline*-4'-*carboxylic acid*, $NO_2 \cdot C_9H_5N \cdot COOH$, prepared by treating cinchonic acid with a mixture of concentrated sulphuric and fuming nitric acids at 60—70°, melts and decomposes at 275—278°; it dissolves with great difficulty in water, dilute acids, and in different organic solvents, but is readily dissolved by hot glacial acetic and concentrated hydrochloric acids. The *barium* salt crystallises in yellow needles, and the *calcium* and *ammonium* salts are also crystalline; the *silver* salt is amorphous. When nitrocinchonic acid is distilled with silver powder, 4-nitroquinoline is produced; reduction with stannous chloride converts it into the anhydride of 4-amidocinchonic acid.

The *anhydride* of 4-amidocinchonic acid, $C_9H_5N{<}^{NH}_{CO}$ or $C_9H_5N{<}^{N}_{C \cdot OH}$, crystallises from water and alcohol in slender yellow needles and melts at 254—255°; it dissolves in cold solutions of caustic alkalis, developing a red coloration, and is precipitated by carbonic anhydride. When boiled with excess of barium hydroxide in a reflux apparatus during 3—4 hours, it yields *barium* 4-amidocinchonate, which forms a yellow, crystalline precipitate; the *acid*, obtained by decomposing the *silver* salt with hydrogen sulphide, crystallises in lustrous red needles.   M. O. F.

Condensation of Semicarbazide with β-Diketones. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1898, [iii], **19**, 77).—Semicarbazide readily interacts with acetylacetone with elimination of $2H_2O$, to form a beautifully crystalline *substance*, $C_6H_9N_2$, which melts at 107—108°, and probably has the structure of a pyrazole derivative, $^{CMe=N}_{CH:CMe}{>}N \cdot CO \cdot NH_2$. It appears probable therefore that the substance, $C_{11}H_{17}N_3O$, melting at 192—193°, which was formerly obtained by acting with semicarbazide on the ketone $C_{10}H_{16}O_2$ (*Compt. rend.*, 1896, **22**, 1422) is not a semicarbazone, but a derivative of the above type.   W. A. D.

Conversion of Secondary Acid Hydrazides into Derivatives of Furodiazole, Pyrrodiazole, and Thiodiazole. By ROBERT STOLLÉ (*Ber.*, 1899, **32**, 797—798).—The secondary acid hydrazides of the type $R \cdot CO \cdot NH \cdot NH \cdot CO \cdot R$, are converted on treatment with dehydrating agents, alcoholic ammonia, or phosphorus pentasulphide into derivatives of furodiazole, pyrrodiazole, or thiodiazole respectively.

Dimethylfurodiazole, $^{N:CMe}_{N:CMe}{>}O$, is obtained by heating diacetyl-

hydrazine (this vol., i, 413) with zinc chloride or phosphoric anhydride; it can also be prepared by heating tetracetylhydrazine. It is a colourless liquid, boiling at 178—179°, and miscible with water, alcohol, or ether, in all proportions.

Dimethylpyrrodiazole, $\begin{array}{c}N:CMe\\ | \\ N:CMe\end{array}$ NH, is prepared by heating di- or tetr-acetylhydrazine with alcoholic ammonia at 200°, or by heating a mixture of diacetylhydrazine and zinc ammonium chloride at 250°. It is a white substance, melts at 141—142°, boils at 159° under 19 mm. pressure, and is easily soluble in water, alcohol, and ether.

Dimethylthiodiazole, $\begin{array}{c}N:CMe\\ | \\ N:CMe\end{array}$ S, obtained by heating diacetylhydrazine with phosphorus pentasulphide, is a white, crystalline solid, melting at 64° and boiling at 89° under 14 mm. pressure; it is readily soluble in water, alcohol, and ether.

From dibenzoylhydrazine, diphenylfurodiazole boiling at 231° under 13 mm. pressure, diphenylpyrrodiazole, Pinner (Abstr., 1897, i, 637), and diphenylthiodiazole were prepared.

Diphenylthiodiazole, $\begin{array}{c}N:CPh\\ | \\ N:CPh\end{array}$ S, crystallises from alcohol in glistening leaflets, melts at 141—142°, boils at 259° under 17 mm. pressure, and is insoluble in water. J. F. T.

Synthesis of Indazoles and Phenotriazines. By A. König and Arnold Reissert (*Ber.*, 1899, **32**, 782—793).—*Orthonitrobenzophenylhydrazide*, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot NHPh$, crystallises from chloroform or alcohol in orange-coloured needles, is only slightly soluble in ether, light petroleum, and water, and melts at 141°; like benzophenylhydrazide, it dissolves in hot caustic soda and ammonia, and is precipitated again by acids; it gives a violet coloration when warmed with concentrated sulphuric acid. The substance also exists in a white modification, and on crystallising from alcohol, both forms usually separate together, but after being for some time in contact with the solution, the white form passes completely into the yellow form. *Orthamidobenzophenylhydrazide* is a colourless base; when acted on with 2 mols. of nitrous acid, it gives an unstable, reddish, crystalline diazo-compound, probably $OH \cdot N_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot NPh \cdot NO$. When this is boiled with alcohol, it loses nitrogen and nitrous acid, and is converted into 1′-*phenylisindazolone*, $C_6H_4 \begin{array}{c}CO\\ \diagdown \\ NPh\end{array} NH$, and a small quantity of 3′-*anilido-β-phenotriazone*, $C_6H_4 \begin{array}{c}CO \cdot N \cdot NHPh\\ \diagdown | \\ N = N\end{array}$, which is separated by its insolubility in caustic soda, crystallises in yellow needles, and melts at 135°.

1′-Phenylisindazolone is stable, crystallises from alcohol in brown needles, melts at 209°, and is fairly soluble in ether and in boiling alcohol, less so in acetone and benzene, and only slightly in water. It is not reduced by sodium in alcoholic solution, and is not attacked by phosphorus pentachloride at 150°; it forms a monobasic, yellowish *sodium* salt which crystallises with $5H_2O$. The *benzoyl* derivative

crystallises in colourless needles and melts at 89°. The *methyl* derivative crystallises from dilute alcohol in long, thin, colourless, glistening, monohydrated needles, and melts at 54—55°; it is insoluble in water, but dissolves in alcohol or ether. When oxidised with potassium permanganate, 1'-phenylisindazolone is converted into *nitrosodiphenylamineorthocarboxylic acid* (orthonitrosoanilidobenzoic acid), $NO \cdot NPh \cdot C_6H_4 \cdot COOH$; this separates from benzene in yellow crystals containing 1 mol. of benzene of crystallisation, dissolves readily in alcohol, ether, and acetone, but only slightly in water and light petroleum, and melts at 120—125°; the *silver* salt is yellow. On reducing it with zinc dust and acetic acid, Graebe and Lagodzinski's phenylanthranilic acid is produced (Abstr., 1892, 1086).

Orthonitrophenylacetanilide, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot NHPh$, crystallises from alcohol in needles, dissolves readily in acetone, only slightly in ether and benzene, is insoluble in water, and melts at 158—159°. *Orthamidophenylacetanilide*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot NHPh$ is produced in small quantity by the reduction of the nitro-compound, oxindole being the chief product; it separates from dilute alcohol and from benzene in colourless crystals and melts at 132°. T. M. L.

Syntheses in the Purine Group. By EMIL FISCHER (*Ber.*, 1899, **32**, 435—504).—This paper is a summary of the results obtained by the author, more particularly in his recent researches. After an historical introduction, the question of the structure and nomenclature of these diureides is considered. They are best regarded, as indeed has been done of late, as derivatives of *purine*, all containing as a nucleus a combination of a metadiazine with an imidazole ring. For purine itself, two tautomeric formulæ are possible:

$$\begin{matrix} N:CH \cdot C \cdot NH \\ \overset{|}{C}H:N \cdot \overset{|}{C}-N \end{matrix} {\Large>} CH \qquad\qquad \begin{matrix} N:CH \cdot C-N \\ \overset{|}{C}H:N \cdot \overset{|}{C} \cdot NH \end{matrix} {\Large>} CH$$
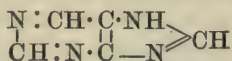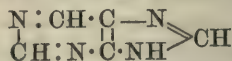
Purine.   Tautomeric formula.

In the case of derivatives, corresponding isomerides actually exist; for example, a 7- and a 9-methylpurine are both known, and similar examples occur frequently, and are always possible, so long as the imidazole ring contains no oxygen. Purine itself is only known in one form; in this and similar cases, where there is no reason to adopt one formula rather than another, formulæ are used corresponding with the first of those given above. For uric acid (trioxypurine), the formula of Medicus has been shown to be most suitable. The tautomeric enolic form would better exhibit the relations of uric acid to the chlorine and ethoxy-derivatives, but the author prefers the old ketonic formula for uric acid itself. For its sulphur analogue (trithiopurine), on the other hand, he prefers the tautomeric formula:

$$\begin{matrix} NH \cdot CO \cdot C \cdot NH \\ CO \cdot NH \cdot C \cdot NH \end{matrix} {\Large>} CO \qquad\qquad \begin{matrix} N:C(SH) \cdot C \cdot NH \\ C(SH):N \cdot C-N \end{matrix} {\Large>} C \cdot SH.$$
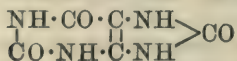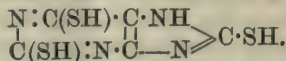
Uric acid (trioxypurine).   Trithiopurine.

These principles are applied throughout in the assignment of formulæ. Of these formulæ, the four next given are of special interest:

$$\begin{array}{l} NH \cdot CO \cdot \underset{||}{C} \cdot NH \\ CO \cdot NH \cdot \underset{}{C} \text{---} N \end{array}\!\!\!>\!\!CH$$

Xanthine (2 : 6-dioxypurine).

$$\begin{array}{l} NH \cdot CO \text{---} \underset{||}{C} \cdot NH \\ C(NH_2) : N \cdot \underset{}{C} \text{---} N \end{array}\!\!\!>\!\!CH$$

Guanine (2-amino-6-oxypurine).

$$\begin{array}{l} NH \cdot CO \cdot \underset{}{C} \cdot NH \\ CH : N \text{---} \underset{}{C} \text{---} N \end{array}\!\!\!>\!\!CH$$

Hypoxanthine (6-oxypurine).

$$\begin{array}{l} N : C(NH_2) \cdot \underset{}{C} \cdot NH \\ CH : N \text{---} \underset{}{C} \text{---} N \end{array}\!\!\!>\!\!CH$$

Adenine (6-aminopurine).
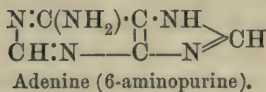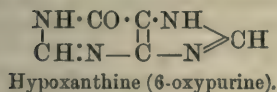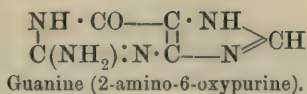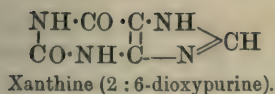
The methods used in synthesising members of the purine group are described as five in number :

(1) The preparation of uric acid from pseudo-uric acid, $CO\!<\!\!\begin{array}{l}NH \cdot CO \\ NH \cdot CO\end{array}\!\!>\!\!CH \cdot NH \cdot CO \cdot NH_2$, and of its alkyl derivatives by an analogous reaction. This conversion is usually effected by boiling with dilute hydrochloric acid (Abstr., 1897, i, 268) ; in the case of ψ-uric acid itself, a great deal of the solvent is necessary, but in the case of its methyl derivatives, this difficulty disappears, and the 1 : 3 : 7-trimethyl derivative is even converted by boiling with water alone.

(2) The methylation of oxypurines. This is best effected by shaking an alkaline solution of the oxypurine with methylic iodide either in the cold or at higher temperatures, for example, 80—90° (this vol., i, 392). In the case of uric acid, 3- and 9-methyl-, 3 : 9-, 1 : 3-, and 7 : 9-dimethyl-, 3 : 7 : 9-trimethyl-, and tetramethyl-uric acids are formed successively.

(3) The conversion of oxypurines into chloropurines by heating them with a mixture of phosphorus oxychloride and pentachloride (Abstr., 1884, 996), or with the oxychloride alone (this vol., i, 175, 176), at temperatures between 130° and 170°, the reaction being facilitated by shaking. The product formed is determined to a large extent by the conditions of the experiment ; 2 : 6 : 8-trioxy-3 : 7-dimethylpurine (dimethyluric acid), for instance, yields 8-chloro-2 : 6-dioxy-3 : 7-dimethylpurine (chlorodimethylxanthine) when heated with phosphorus oxychloride, whilst with a mixture of oxychloride and pentachloride at 140° it yields 6-chloro-2 : 6-dioxy-3 : 7-dimethylpurine, and with excess of pentachloride at 170°, 2 : 6 : 8-trichloro-7-methylpurine, one methyl group being eliminated.

(4) Conversion of the halogen purines into oxy-, thio-, and amido-purines. The conversion into oxypurines can be effected by heating with aqueous alkali (Abstr., 1897, i, 642) ; but if a partial break-down of the purine nucleus occurs, alcoholic potash may be used with advantage ; this reacts at a comparatively low temperature, and produces alkoxy-derivatives (Abstr., 1897, i, 642). Concentrated hydrochloric acid at 125—130° is an even more efficient agent (Abstr., 1896, i, 14) ; an 8-chlorine atom is often removed most readily ; sometimes, however, it remains persistently (Abstr., 1898, i, 180), whereas chlorine in another position is readily removed (this vol., i, 392). Aqueous potassium hydrosulphide effects the conversion of halogen into thio-derivatives with comparative readiness (Abstr., 1898, i, 340) ; the temperature employed was usually 100°, occasionally 120°. Alcoholic ammonia, at temperatures up to 150°,

effects the replacement of the halogen by the amido-group; no break-ing down of the purine nucleus takes place in this case, and it is only small in amount when aqueous ammonia, which reacts rather more vigorously, is used. Diamido- but not triamido-derivatives can be prepared in this way, and by the action of nitrous acid a ready conversion into oxy-derivatives can often be effected.

(5) Reduction of the halogen purines, often by means of fuming hydriodic acid and phosphonium iodide (Abstr., 1884, 996). When no oxygen is present in the molecule, the yield is poor, however, and in this case it is better to treat with concentrated hydriodic acid at 0°, when, as a rule, some halogen is replaced by hydrogen, but some at the same time by iodine, and then to boil the resulting iodo-compound with zinc dust and water, when the iodine is replaced by hydrogen; in this way, 2 : 6 : 8-trichloropurine can be converted successively into 2 : 6-di-iodopurine and purine itself (this vol., i, 175). Boiling with zinc dust and water, to which a little ammonia may sometimes be added with advantage, also effects a partial replacement of chlorine by hydrogen; 2 : 6 : 8-trichloro-9-methylpurine yields 2-chloro-9-methylpurine, and 2 : 6 : 8-trichloro-7-methylpurine and 2 : 6-dichloro-7-methylpurine yield 2-chloro-7-methylpurine (this vol., i, 175).

There follows next a recapitulation of the more important purine derivatives, with their methods of preparation and properties.

After this, a number of decompositions of these purine compounds, observed for the first time by the author and his collaborators, and involving a breaking down of the purine nucleus, are enumerated; but first three decompositions, long known, are mentioned as of particular utility in determining the constitution of purine deri-vatives : (1) the formation of alloxan, recognised by the murexide test ; heating with nitric acid effects this only in the case of the uric acids, amidodioxypurines and some halogen-xanthines, and then only with difficulty in some cases; aqua regia effects it in the case of xanthines, and some thio-derivatives ; 2 : 8- and 6 : 8-dioxypurines ; the monoxypurines, the oxydichloropurines, and all derivatives which contain a CH-group in the alloxan nucleus fail to give the reaction ; (2) the formation of sarcosine, on heating with strong hydrochloric acid at 170—200°, which proves the presence of a 7-methyl group ; (3) the formation of guanidine or a methylguanidine, recognised by means of their picrates, on treatment with hydrochloric acid and potassium chlorate; this did not happen in the case of 8-amino-2 : 6-dioxy-7-methylpurine, although it might have been expected to take place.

As regards the influence of constitution on properties, it is found that the introduction of oxygen, sulphur, or the amido-group lessens the solubility in water and raises the melting point. The introduction of methyl groups increases the solubility, volatility, and power of crystallising, and lowers the melting point. The oxidisability by nitric acid, or by chlorine and water, increases with the number of oxygen atoms or amido-groups present ; it is sometimes lessened by the presence of methyl groups. The oxidisability by ammoniacal silver solution is also lessened by methyl, especially in the 7-position The conversion of a ψ-uric into a uric acid is facilitated by the presence

of methyl, especially in the 7-position. The action of the chlorides of phosphorus varies considerably with the number of methyl groups present ; and the breaking down of the purine nucleus by alkalis, as well as the elimination of halogens by aqueous or alcoholic alkali, is most readily effected in the case of those derivatives in which all the acid hydrogen has been replaced by methyl.

Finally, a list is given of all the compounds prepared by the author and his collaborators, together with a few that occur naturally, or have been prepared by other investigators. C. F. B.

Influence of Water on the Addition of Ethylenic Oxide to Ammonia and Amines. By LUDWIG KNORR (*Ber.*, 1899, **32**, 729—732).—Acetalamine which has been dried over barium oxide does not react with ethylene oxide at the ordinary temperature, but in presence of water (1 mol.), complete combination occurs ; the product, on distillation, gives off water, and on repeated fractionation yields a substance boiling at 253—255° under atmospheric pressure, which is probably 5-*ethoxymorpholine*, $\mathrm{NH}{<}^{\mathrm{CH_2 \cdot CH(OEt)}}_{\mathrm{CH_2 \underline{\quad\quad} CH_2}}{>}\mathrm{O}$. When methylacetalamine is used, the behaviour is similar, and the product finally obtained is doubtless 1-*methyl-3-ethoxymorpholine*, $\mathrm{NMe}{<}^{\mathrm{CH_2 \cdot CH(OEt)}}_{\mathrm{CH_2 \underline{\quad\quad} CH_2}}{>}\mathrm{O}$.

Ammonia, methylamine, and ethylamine, which, as a rule, act violently on ethylenic oxide, react with it only very slowly when quite dry, or not at all. Dry di-isobutylamine does not attack it at 85°, but in presence of water, combination occurs at the ordinary temperature. With diamylamine, interaction does not occur at 85°, but at 150° hydroxydiamylamidoethylic alcohol is formed.

The interaction of ammonia and ethylenic oxide is not due to the addition to the latter of $\overset{+}{\mathrm{NH_4}}$ and $\overset{-}{\mathrm{OH}}$, which are usually assumed to be the ions present in an aqueous solution of ammonia, but apparently to the addition of $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{NH_2}}$ or of $\overset{+}{\mathrm{H}}$ and $\mathrm{NH_3}\cdot\overset{-}{\mathrm{OH}}$. The concentration of the hydrogen ions in a solution of ammonia, however, cannot be greater than in water, owing to the presence of $\overset{-}{\mathrm{OH}}$ ions, hence it must be supposed that the ion $\overset{-}{\mathrm{NH_2}}$ or $\mathrm{NH_3}\cdot\overset{-}{\mathrm{OH}}$ is present in the solution in addition to $\overset{-}{\mathrm{OH}}$ and $\overset{+}{\mathrm{NH_4}}$.

With this assumption, the behaviour of ethylenic oxide in a solution of ammonia may be explained by one of the following equations :

$$\overset{\mathrm{CH_2}}{\underset{\mathrm{CH_2}}{|}}{>}\mathrm{O} + \overset{\overset{-}{\mathrm{NH_2}}}{\underset{\overset{+}{\mathrm{NH_4}}}{}} = \overset{\mathrm{CH_2 \cdot NH_2}}{\underset{\mathrm{CH_2 \cdot ONH_4}}{|}} = \overset{\mathrm{CH_2 \cdot NH_2}}{\underset{\mathrm{CH_2 \cdot OH}}{|}} + \mathrm{NH_3},$$

or

$$\overset{\mathrm{CH_2}}{\underset{\mathrm{CH_2}}{|}}{>}\mathrm{O} + \overset{\overset{-}{\mathrm{NH_3}}\cdot\mathrm{OH}}{\underset{\overset{+}{\mathrm{NH_4}}}{}} = \overset{\mathrm{CH_2 \cdot NH_3 \cdot OH}}{\underset{\mathrm{CH_2 \cdot ONH_4}}{|}} = \overset{\mathrm{CH_2 \cdot NH_3 \cdot OH}}{\underset{\mathrm{CH_2 \cdot OH}}{|}} + \mathrm{NH_3}.$$
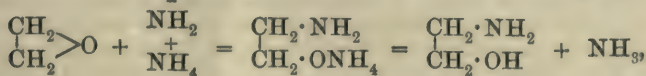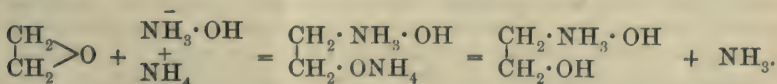
A. L.

**Breaking-down of Phenomorpholine by Exhaustive Methyl-
ation.** By LUDWIG KNORR (*Ber.*, 1899, **32**, 732—736).—Griess
observed that the methylhydroxide of orthodimethylamidoanisoil, when
heated, breaks down into methylic alcohol and dimethylanisidine
(Abstr., 1880, 638), and in similar manner, as shown by Königs and
Feer (Abstr., 1885, 1245), dimethyltetrahydroquinolium hydroxide
yields kairoline at 150°. The authors find that a similar decom-
position occurs when dimethylphenomorpholinium iodide is heated
with strong soda, the product obtained being dimethylorthamido-
phenylic vinylic ether.

Dimethylphenomorpholinium iodide, $C_{10}H_{14}NOI$, separates in the form
of hard prisms when a mixture of equal parts of methylphenomorpholine,
methylic alcohol, and methylic iodide is left overnight ; it decomposes
indefinitely at 200°.

Dimethylorthamidophenylic vinylic ether, $C_{10}H_{13}NO$, forms a mobile,
colourless oil having a pungent odour and neutral reaction ; it is
scarcely soluble in water, dissolves readily in the usual organic
solvents, and boils at 224—225°. It behaves towards litmus, gold
chloride, ammoniacal silver nitrate, ferric chloride, diazobenzene
chloride, and nitrous acid in much the same manner as does methyl-
phenomorpholine. The *methiodide,* $C_{11}H_{16}NOI$, crystallises in rounded
aggregates; the *picrolonate,* $C_{10}H_{13}NO,C_{10}H_8N_4O_5$, crystallises in slender
needles when its hot alcoholic solution is slowly cooled, and melts at
145—146°. The *picrolonate* of *methylphenomorpholine,* $C_{19}H_{19}N_5O_6$,
separates from hot alcohol as a heavy, crystalline, sandy powder, and
melts at 164—165°.   A. L.

**Breaking-down of the Morpholine Ring by Exhaustive
Methylation.** By LUDWIG KNORR and HERMANN MATTHES (*Ber.*,
1899, **32**, 736—742).—*Dimethylamidoethylic vinylic ether,*
$$NMe_2 \cdot CH_2 \cdot CH_2 \cdot O \cdot CH{:}CH_2,$$
is made by acting on methylmorpholine methiodide in concentrated
aqueous solution with freshly precipitated silver oxide and subjecting
the product to fractional distillation. Aldehyde is at first observed as
a decomposition product, but the amount produced gradually decreases,
and finally a concentrated, strongly alkaline solution of the vinylic
ether distils over, from which the ether may be isolated by extraction
with ethylic ether and distillation over caustic soda. It forms a colour-
less, mobile liquid having an odour resembling that of dimethylethanol-
amine [dimethylamidoethylic alcohol] and methylmorpholine ; it boils
at 124° under 740 mm. pressure, is miscible in all proportions with
water, alcohol, and ether, is very volatile, and distils readily in
steam or ether vapour. Its aqueous solution gives precipitates with
many alkaloidal reagents. The *picrate,* $C_6H_{13}NO,C_6H_2N_3O_7$, crystal-
lises in light yellow, orthorhombic tablets, melts at 85°, and dissolves
readily in water and alcohol. The *picrolonate* $C_6H_{13}NO,C_{10}H_8N_4O_5$,
crystallises from hot dilute alcohol in small, shining, brownish-yellow
cubes, dissolves somewhat sparingly in water but readily in alcohol,
and melts and decomposes at 138°. The *hydrochloride* is hygroscopic,
but may be obtained in long, compact needles ; the *aurichloride,*

$C_6H_{13}NO,HAuCl_4$, crystallises from hot water in delicate, bright yellow, sparingly soluble needles; the *platinochloride*, $(C_6H_{13}NO)_2,H_2PtCl_6$, is readily soluble in water, and separates on addition of alcohol to its aqueous solution as a pale yellow precipitate; the *methiodide* of dimethyl-amidoethylic vinylic ether, $NMe_3I \cdot CH_2 \cdot CH_2 \cdot O \cdot CH:CH_2$, crystallises from a mixture of ether and methylic alcohol in small, compact crystals which are octahedra or combinations of octahedra and rhombic dodecahedra. When it is heated in aqueous solution with moist silver oxide and the product submitted to distillation, a polymeride of divinylic ether is deposited, and a mixture of trimethylamine and acetylene is given off, together with a substance, possibly divinylic ether, which may be obtained on neutralising the distillate with hydrochloric acid and distilling once more; the supposed divinylic ether forms a mobile liquid which burns with a blue, non-luminous flame and forms an explosive mixture with air. A. L.

Decomposition of Naphthalanmorpholine by Exhaustive Methylation: Constitution of Morphine. By LUDWIG KNORR, (*Ber.*, 1899, **32**, 742—749).—*Naphthalanmorpholine*,

$$C_6H_4 \begin{cases} CH_2 \cdot CH-O-CH_2 \\ CH_2 \cdot CH \cdot NH \cdot CH_2 \end{cases},$$
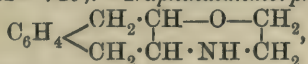
may be obtained from tetrahydronaphthalene oxide by uniting it with amidoethylic alcohol, and treating the resulting *hydroxyethylamido-tetrahydro-β-naphthol* with condensing agents. Its constitution is analogous to that of morphine, which the author (Abstr., 1889, 905) represents by the formula, $OH \cdot C_{10}H_{13} \begin{cases} CH(OH) \cdot CH-O-CH_2 \\ CH_2-CH \cdot NMe \cdot CH_2 \end{cases}$.

Naphthalanmorpholine is a strong, alkaloid-like, stable base which is not altered by distillation under atmospheric pressure, has a neutral reaction, yields well-crystallised salts, and is precipitated from very dilute solution by most alkaloidal reagents. Its N-alkyl derivatives are very active physiologically, and closely resemble morphine in their effect on the human system.

Naphthalanmorpholine may be converted into the *methiodide* of *methylnaphthalanmorpholine*, which is readily converted into *dihydro-β-naphthylic dimethylamidoethylic ether*, and the latter into naphthalene and dimethylamidoethylic alcohol, in accordance with the scheme

$$C_6H_4 \begin{cases} CH_2 \cdot CH-O-CH_2 \\ CH_2 \cdot CH \cdot NMe_2I \cdot CH_2 \end{cases} \rightarrow C_6H_4 \begin{cases} CH_2CH \cdot O \cdot (CH_2)_2 \cdot NMe_2 \\ CH:CH \end{cases}$$

$$\rightarrow C_6H_4 \begin{cases} CH:CH \\ CH:CH \end{cases} + OH \cdot CH_2 \cdot CH_2 \cdot NMe_2,$$
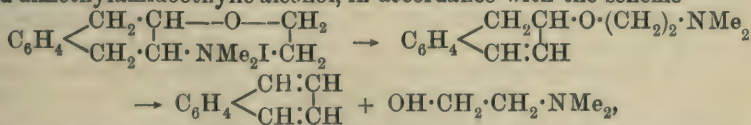
a decomposition exactly analogous to that of codeine into methyl-morphomethine, and finally into methyldihydroxyphenanthrene and dimethylamidoethylic alcohol. A remarkable point of difference, however, is found in the extraordinary readiness with which dihydro-β-naphthylic ether undergoes the secondary change, it being merely necessary to treat the aqueous solution of the substance with 1 per cent. hydrochloric acid in order to effect an immediate separation of naphthalene. This fact supplies an explanation of many changes which have been observed in the study of certain alkaloids, and

illustrates the great readiness shown by many dihydrogenised benzenoid compounds to revert to true aromatic systems. Thus the production of thebenine and morphothebaine from thebaine by the action of dilute or strong hydrochloric acid is probably due to the presence of the morpholine group in attachment to a dihydrogenised nucleus. The relatively great difficulty observed in breaking up methylmorphomethine into hydramine and a phenanthrene derivative would therefore appear to exclude the supposition that methylmorphomethine is a derivative of orthodihydrophenanthrene.

As methylmorphomethine contains three asymmetric carbon atoms, which can only be explained on the supposition that they exist as $>$CH·OH or $>$CH·O·$(CH_2)_2$·NMe$_2$, it must be assumed that the substance is a paradihydrophenanthrene derivative; moreover, as Vongerichten has recently shown that morphol yields phthalic acid on oxidation (this vol., i, 307), the methoxy-group of methylmorphomethine is attached to the dihydrogenised benzene nucleus. The formulæ which best explain the behaviour of methylmorphomethine are

$$\begin{array}{l} \text{CH:CH·C·CH(O·CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2)\cdot\text{CH*} \\ \text{C}_6\text{H}_4\text{——C·CH(OH)————————C·OH*} \quad \text{and} \end{array}$$

$$\begin{array}{l} \text{CH:CH·C·CH(OH)—————CH*} \\ \text{C}_6\text{H}_4\text{——C·CH(O·C}_2\text{H}_4\cdot\text{NMe}_2)\cdot\text{C·OH*'} \end{array}$$
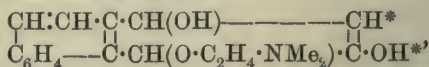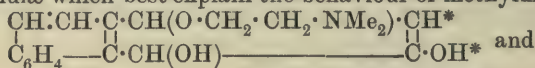
the corresponding formulæ for morphine being

$$\begin{array}{l} \text{NMe·C}_2\text{H}_4\cdot\text{O} \\ \text{CH}_2\cdot\text{CH·C——·CH · CH*} \\ \text{C}_6\text{H}_4\text{——C·CH(OH)·C·OH*} \end{array} \quad \text{and} \quad \begin{array}{l} \text{CH}_2\cdot\text{CH}_2\cdot\text{C·CH(OH)·CH*} \\ \text{C}_6\text{H}_3\text{——C·CH———C·OH*,} \\ \text{NMe—C}_2\text{H}_4\cdot\text{O,} \end{array}$$
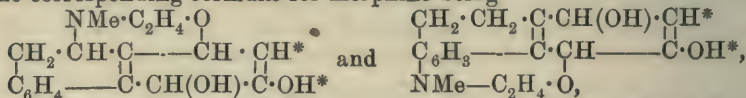
the ethanolmethylamine residue being attached to two carbon atoms in the peri-position, and not in an ortho-position, as has hitherto been assumed. Of these two formulæ for morphine, the author prefers the former, which bears a striking resemblance to that proposed for papaverine by Goldschmidt.

The dihydro-β-naphthylic dimethylamidoethylic ether is made by boiling methylnapthalanmorpholine methiodide with 10 per cent. soda whilst steam is passed through the hot liquid; it is extracted from the distillate by cooling, separating the naphthalene by filtration, and extracting the filtrate with ether. It forms a somewhat mobile oil, is alkaline to moist litmus, and forms a *methiodide* which crystallises in rounded aggregates and decomposes at 140°. It dissolves readily in most of the usual organic media, but is only sparingly soluble in water. In very dilute aqueous solution, it does not yield precipitates with alkaloidal reagents. When the substance is warmed with strong soda, it breaks up gradually into naphthalene and hydramine, and the same decomposition is effected quantitatively in a few moments by mineral acids, and goes on more slowly when organic acids are used.

A. L.

Cevadine [Veratrine]. By MARTIN FREUND and HEINRICH P. SCHWARZ (*Ber.*, 1899, **32**, 800—806).—Commercial cevadine [veratrine], when recrystallised from alcohol, does not melt at 205° as stated by E.

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* There is at present no evidence as to which of these positions is occupied by the OH-group.

Schmidt (Abstr., 1878, 516), but softens at 110° and gradually passes into a transparent resin; this is due to the fact that the alkaloid combines with alcohol of crystallisation, which is lost either on drying at 130—140° or on boiling with water, the pure substance then melting at 205°.

On treatment with alcoholic potassium hydroxide, veratrine is resolved into a base cevine (Wright and Luff, Trans., 1878, **33**, 328) and a mixture of angelic and tiglic acids. Cevine, $C_{27}H_{43}NO_8 + 3\frac{1}{2}H_2O$, separates from water containing a little alcohol in well formed crystals belonging to the triclinic system; the water of crystallisation is given off at 105—110°, and the anhydrous substance softens at 155—160°, becomes a transparent resin at 165—170°, and melts at 195—200°. It reduces ammoniacal silver nitrate and Fehling's solution. On treatment with alcoholic potassium hydroxide, it yields the *potassium* compound, crystallising in slender needles which darken at 240° and decompose at 246°; the *sodium* compound, prepared by treating the base with strong aqueous sodium hydroxide, decomposes at 260—265°; the *hydrochloride* forms beautiful needles melting at 240°; the *methiodide* separates from its alcoholic solution on addition of ether in crystals melting at 240—250°.

The paper concludes with a description of the physiological properties of veratrine and cevine. J. F. T.

Reducing Substances obtained from Egg-albumin. By John Seemann (*Chem. Centr.*, 1898, ii, 1271; from *Diss. Marburg*).—The carbohydrate substance (compare Müller, *Sitz-Ber. ges. Naturw. Marburg*, 1898, 117) is isolated from white of egg, by treating 25 grams of the substance, free from ovimucoid, with 400 c.c. of very dilute alkali, and then adding 100 c.c. of hydrochloric acid of a concentration such that the mixture shall contain 2—3 per cent. of the acid. After passing steam through the hot liquid, titration with Fehling's solution showed a content of 9 per cent. of a reducing substance calculated as dextrose; from ovimucoid, 30·9 per cent. was obtained. This substance was identified as glucosamine (chitosamine). E. W. W.

Formation of Sugar from Albumin. By Ferdinand Blumenthal *Compt. rend.*, 1899, **128**, 117—120).—When egg-albumin is dissolved in water, mixed with sodium or barium hydroxide solution, and after an hour or two is acidified with hydrochloric acid, boiled, neutralised with sodium hydroxide, re-acidified with acetic acid, evaporated to dryness, and extracted with hot alcohol of 93 per cent., it yields a hexose which has the general properties of a glucose, and after removal of albumoses and peptones, is slightly lævogyrate, even after allowing for the possible presence of small quantities of albumoses. It is not fermented by beer-yeast, and hence would seem to be levulose; the quantity obtained amounts to from 8 to 12 per cent. of the albumin. C. H. B.

Formation of Sugar from Albumin. By Ferdinand Blumenthal and Paul Mayer (*Ber.*, 1899, **32**, 274—278).—When purified white of egg is boiled with dilute hydrochloric acid, a liquid is

obtained which yields an osazone having the composition of glucosazone; this melts at 200—205°, but is not lævorotatory in acetic acid solution. Similar results are obtained with the albumin from the yolk of egg after extracting the fat with ether and washing with water and alcohol; the osazone obtained in this case melts at 203°, and is lævorotatory in acetic acid solution. Both osazones appear to be somewhat impure glucosazone. It seems probable that the separation of the carbohydrate is not accompanied by destruction of the albumin molecule, and that the residue still belongs to the class of albumins.   A. H.

Crystallised Fibrin. By A. MAILLARD (*Compt. rend.*, 1899, **128**, 373—375).—Some tubes of antidiphtheric serum several months old were found to contain a deposit of fibrin in small, angular crystals which acted on polarised light and seemed to belong to the monoclinic system. These crystals gave all the ordinary reactions of fibrin. Similar crystals were obtained from ordinary ox serum, and the author adopts the view that whether fibrin is crystalline or amorphous depends mainly on the rate at which it separates from the liquid in which it is formed.   C. H. B.

Proteid of Wheat-gluten. By KURATA MORISHIMA (*Chem. Centr.*, 1898, ii, 1102; from *Arch. exp. Path. Pharm.*, **41**, 345—354). —According to the author, wheat-gluten contains only one proteid, *artolin*, which is prepared by extracting with dilute alkali, precipitating with dilute acid, and purifying by dissolving it in water or dilute alcohol, and precipitating with absolute alcohol and ether. From concordant analyses of several preparations, the formula $C_{185}H_{288}N_{50}SO_{58},2HCl$ is ascribed to the hydrochloride. Artolin is slightly soluble in cold, but more easily soluble in hot, water, and the hot solution, on cooling, becomes turbid; it is easily soluble in very dilute mineral acids, in alkalis, in a large volume of acetic acid, and in moderately dilute alcohol; it is precipitated from its alcoholic solution by adding a large quantity of absolute alcohol or of water.

The portion of the gluten which is insoluble in dilute alkali is very rich in phosphorus.   E. W. W.

The Proteid-like Substances of Silk. By G. WETZEL (*Zeit. physiol. Chem.*, 1899, **26**, 535—542).—Fibroin, silk-gelatin, and conchiolin yield, with acids, basic materials similar to the protamines. In the case of fibroin, the yield is a small one.   W. D. H.

Glutolin, a Proteid of Blood-serum. By EDWIN S. FAUST (*Chem. Centr.*, 1898, ii, 1105; from *Arch. exp. Path. Pharm.*, **41**, 309—324).—Glutolin, $C_{204}H_{336}N_{60}SO_{70}$, is obtained by adding an equal volume of a saturated solution of ammonium sulphate to the serum of horse blood, dissolving the precipitate in a large quantity of water, making the solution feebly acid with acetic or hydrochloric acid, and then saturating the solution with carbonic anhydride. The precipitate, which is generally plastic like dough, is kneaded with a 10 per cent. solution of sodium chloride, and then treated with a 0·5 per cent. solution of potassium hydroxide. The filtrate, when neutralised with hydrochloric acid, yields a flocculent precipitate of

glutolin which does not contain serum-globulin, for it does not turn alkaline lead solutions black on boiling ; it is insoluble in solutions of neutral salts, soluble in alkali hydroxides and ammonia, gives the biuret reaction in the cold, and Millon's reaction faintly. Glutolin belongs to the glutins, and like glutin, when decomposed with hydrochloric acid, yields glycocine, which was identified by converting it into hippuric acid ; the other proteids of blood do not give this reaction. The author regards glutolin as a compound intermediate in composition between albumin and glutin, and as the parent substance from which the glutinous portion of the tissue is derived.

E. W. W.

Nucleins. By ALBERT NEUMANN (*Chem. Centr.*, 1898, ii, 1211 ; from *Arch. Anat. Phys.*, 1898, 374—378).—According to the author, nucleic acid consists of three acids, a- and b-nucleic acids and nucleothymic acid. The a- differs from the b-nucleic acid in that 5 per cent. solutions of its salts gelatinise, whilst those of the b-acid do not. Nucleothymic acid, which is a nuclein, since it contains phosphorus, carbohydrates, and alloxuric bases, is also formed by hydrolysing a- or b-nucleic acid, and, unlike thymic acid, is precipitated by hydrochloric acid. The alloxuric bases formed by decomposing a- and b-nucleic acids give the xanthine reaction with nitric acid and sodium hydroxide solution, whilst those obtained from nucleothymic acid do not give this reaction. All three acids give Tollens' pentose reaction with phloroglucinol and hydrochloric acid. In order to test for nucleins, acetic acid is added to the cold solution, whereby the nucleins containing albumin are precipitated ; the nucleins which do not contain albumin are then thrown down by hydrochloric acid, and the acid mixture boiled until the precipitate is dissolved. The solution gives a cherry-red coloration with phloroglucinol and concentrated hydrochloric acid, and when warmed with an excess of ammonia and silver nitrate, forms a flocculent precipitate of alloxuric silver compounds. The phosphoric acid in nucleins is determined by treating the ash with sodium carbonate and nitric acid. The three nucleic acids are easily dissolved, but not attacked by the alkaline digestive juices. When administered to a dog, four-fifths are eliminated in the urine, and one-fifth in the fæces. Nucleic acid, when administered per os, or nucleothymic acid when subcutaneously injected, in a few hours causes strong hyperleucocytose which is not preceded by hypoleucocytose, but the sodium salts of these acids do not produce this result, the author experiencing no effects from a dose of 10 grams. E. W. W.

Action of Hydrogen Sulphide and Acids on Blood-pigment. By ERICH HARNACK (*Zeit. physiol. Chem.*, 1899, 26, 558—585).— Hæmoglobin free from oxygen is not affected by hydrogen sulphide alone, but it is if previously saturated with carbonic anhydride. The new substance formed is of a dark-red colour, and shows a characteristic absorption band in the orange ; it is termed sulph-hæmoglobin, and is considered to be a compound of the pigment with hydrogen sulphide. By dilute acid, it is broken up into hydrogen sulphide and acid-hæmoglobin. W. D. H.

Colouring-matters of Blood and Bile. By WILLIAM KÜSTER (*Ber.*, 1899, **32**, 677—682).—Dibasic hæmatic acid, $C_8H_{10}O_5$, was stated to be obtained by oxidising hæmatin (Abstr., 1896, i, 516) or hæmatoporphyrin (Abstr., 1897, i, 232) with sodium dichromate in acetic acid solution. It is now shown that the same product is obtained, whether the source of the hæmatin be the blood of oxen, horses, or sheep, but that it contains nitrogen, and is identical with the biliverdic acid, $C_8H_9NO_4$, obtained by the oxidation of the bilirubin of gall-stones (Abstr., 1897, i, 647). When warmed with sodium hydroxide solution, it loses ammonia, and yields the anhydride of tribasic hæmatic acid, $C_8H_8O_5$, an exchange of the NH-group for oxygen taking place. *Calcium biliverdate*, $(C_8H_8NO_4)_2Ca + H_2O$, is obtained by treating an aqueous solution of the acid with calcium carbonate at the ordinary temperature, and leaving the solution to evaporate spontaneously; as the anhydride, $C_8H_8O_5$, may be formed to some extent, it is better to extract the solution with ether before evaporating it, otherwise the calcium salt crystallises with difficulty. It is just possible that this acid is a mixture of isomerides.

The anhydride of tribasic hæmatic acid melts at 97—98° when pure; the corresponding *silver* salt has the composition $C_8H_7Ag_3O_6 + \frac{1}{2}H_2O$; by treatment with cold water and calcium carbonate, a solution is obtained from which a basic calcium salt is precipitated when heat is applied. When reduced with hydriodic acid, it yields a tribasic *acid*, $C_8H_{12}O_6$, which is stable towards permanganate; possibly this is a mixture of isomerides.   C. F. B.

Formation of Melanin-like Pigments from Proteids. By RUSSELL H. CHITTENDEN and ALICE H. ALBRO (*Amer. J. Physiol.*, 1899, **2**, 291—305).—The possibility of the relationship of the melanins to anti-albumid was first pointed out by Schmiedeberg on account principally of the high percentage of carbon in both. In the present research, the hydrolytic cleavage of anti-albumid produced by prolonged boiling with sulphuric acid gave rise to a black pigment with a higher percentage of carbon than in the original substance; this pigment is soluble in alkalis and can be precipitated by acetic acid. Hemipeptone, treated in the same way, yields a similar pigment, with a different percentage composition. The artificial melanins resemble, therefore, the natural ones in being numerous.   W. D. H.

Organic Chemistry.

The Negative Nature of Unsaturated Groups of Atoms. By FERDINAND HENRICH (*Ber.*, 1899, **32**, 668—676. Compare Abstr., 1898, i, 631).—The ethylene group, ·CH:CH·, appears to be negative in character; that is to say, it confers replaceability on the hydrogen atoms of a CH$_2$-group when this radicle is attached to it as well as to a CO-group. These hydrogen atoms in diethylic glutaconate, COOEt·CH:CH·CH$_2$·COOEt, can be replaced successively by methyl, by dissolving the substance in alcoholic sodium ethoxide and adding methylic iodide to the solution. *Dimethylglutaconic acid* melts at 129—130°, and undoubtedly has both the methyl groups attached to the same carbon atom, since it is oxidised by permanganate to dimethylmalonic acid, and does not react with nitrous acid. Further, ethylic glutaconate condenses with diazobenzene chloride, with benzaldehyde and sodium ethoxide, and also with acetaldehyde in the presence of diethylamine.

It is pointed out that the acetylene group, ·C:C·, is more strongly negative than the ethylene group, ·CH:CH·; further, that the group ·CH:N· is also negative, possibly more so than ·CH:CH·; and that ·C:N is certainly more negative than ·C:C·. The azo-group ·N:N· is negative in amidoazobenzene and its dinitro-derivative; still more so in azoimide. In all these radicles, and in the ordinary negative groups ·CHO, ·COOEt, ·CRO, ·CO·CO·COOEt, &c., atoms of like or unlike kinds occur linked together by double or triple bonds, and the author concludes that "a negative radicle thus appears to be characterised by—indeed its negative character appears to be a consequence of—the occurrence in the radicle of like or unlike atoms in intimate union, that is, doubly or triply linked to each other." C. F. B.

Electronegative Character of certain Unsaturated Organic Radicles. By ERNEST CHARON (*Compt. rend.*, 1899, **128**, 736—739). —The author regards the group R·CH:CH· as a radicle having well marked electronegative characters, and bases this opinion on (1) the formation of a large proportion of pinacone by the reduction of crotonaldehyde, the quantity of pinacone found in such reactions being greater the more pronounced the electronegative character of the molecule; (2) the ready formation of crotonylic bromide, chloride, and iodide by action of the halogen hydracids on crotonylic alcohol; (3) the unstability of crotonylic iodide when exposed to light, as compared with the stability of allylic iodide. Henrich's observation, that in phenylic ethylic glutaconate, COOPh·CH:CH·CH$_2$·COOEt, both hydrogen atoms of the CH$_2$-group are readily replaced by an alkylic group, affords further confirmation of this view. C. H. B.

Action of Zinc Dust on Dibromides, C$_n$H$_{2n}$Br$_2$, in Alcoholic Solution. By WLADIMIR IPATIEFF (*Chem. Centr.*, 1898, ii, 472; from *J. Russ. Chem. Soc.*, 1898, **30**, 292—297).—By the action of zinc dust on dibromides in which the bromine atoms are not united to con-

tiguous carbon atoms, closed chain hydrocarbons are obtained, whilst with those containing the bromine united to adjacent carbon atoms, olefines are formed. By the action of zinc dust on dibromo-β-dimethylethylene, prepared from dimethylallene (*J. Russ. Chem. Soc.*, 27, 387), however, a hydrocarbon which boils at 35—38° and has a composition corresponding with that of trimethylethylene, is formed. This substance combines with bromine forming dibromotrimethylethylene, from which, by the action of alcoholic potassium hydroxide, an unsaturated compound, C_5H_9Br, is obtained. Dibromotrimethylethane, prepared from bromine and dimethylethylcarbinol (*J. Russ. Chem. Soc.*, 27, 374), when treated with zinc dust, yields trimethylethylene, from which dibromisopropylethane, $CHMe_2 \cdot CHBr \cdot CH_2Br$, is obtained by the action of bromine; the latter is also prepared by the action of bromine on isopropylethylene (*J. Russ. Chem. Soc.*, 1877, 151) boils at 64—66°, has a sp. gr. 1·7162 at 0°, and when treated in alcoholic solution with zinc dust yields pure isopropylethylene. E. W. W.

Action of Bromine on Ethylic Bromide in Presence of Aluminium Bromide. By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, 19, [iii], 497—499).—A detailed account of work already published (compare this vol., i, 1). G. T. M.

Action of Aluminium Chloride on Acetylene Tetrachloride. By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, 19, [iii], 499—500). —When acetylene tetrachloride is heated to 110° in the presence of aluminium chloride, hydrogen chloride is evolved, carbon deposited, and a certain quantity of the isomeric unsymmetrical tetrachlorethane produced; dichloracetylene could not be detected, and the deposition of carbon is probably due to the decomposition of this substance.

G. T. M.

Action of Bromine on Acetylene Tetrachloride in Presence of Aluminium Chloride. By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, 19, [iii], 500—502).—Contains details of a reaction previously studied (compare Abstr., 1898, i, 614). G. T. M.

Thio-derivatives obtained by the Action of Aluminium Haloids on Organic Compounds. Synthesis of Thiocarbonates. By MICHAËL I. KONOWALOFF (*Chem. Centr.*, 1898, ii, 361—362; from *J. Russ. Chem. Soc.*, 1898, 30, 12—22).—When a solution of aluminium bromide in carbon bisulphide is mixed with ethylenic bromide in a closed tube, the mixture becomes turbid in 10—30 minutes, a heavy, brown oil separates, and after a time forms a crystalline mass. The reaction takes place without development of heat or liberation of gas. The liquid portion is separated, and the crystals of the *compound*, $AlBr_3, C_2H_4Br_2, CS_2$, are washed with ethylenic bromide and dried at 50—60° in a stream of carbonic anhydride; they fume in the air, becoming opaque, and, when heated, are not affected below 120°, but melt and decompose at 137—138°. This compound is almost insoluble in organic solvents, and very slightly soluble in acetic chloride; it reacts energetically with water, forming ethylenic dithio-carbonate, $CO{<}^S_S{>}C_2H_4$, melting at 33—34° (Gusemann gave 31°),

and, with alcoholic ammonia, yielding thioethylenic glycol and carbamide.

When a solution of aluminium bromide in carbon bisulphide is treated with ethylic bromide, the compound $(AlBr_3,EtBr)_2,CS_2$ separates after 7 days as a heavy oil, which, by the action of water, yields diethylic dithiocarbonate, $CO(SEt)_2$.

Propylic bromide, bromoform, propylenic bromide, and tribromopropane react with aluminium bromide and carbon bisulphide in a similar manner, and with amylenic bromide there is a violent reaction, with liberation of hydrogen bromide.

Carbon bisulphide combines, but much more slowly, with aluminium chloride and ethylenic chloride, and also with aluminium iodide and methylic or ethylic iodide.   E. W. W.

Synthesis of Ethylic Alcohol. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, **128**, 862—864).—It has been stated that alcohol was first synthesised from ethylene by Hennell in 1828 ; this, however, is not the case. From sulphuric acid which had absorbed ethylene, Hennell simply obtained a potassium salt which resembled the potassium ethylic sulphate obtained by him from alcohol ; no analysis of the salt was given, however, nor was alcohol regenerated from it. The author first effected this synthesis, and showed that the alcohol obtained from pure ethylene and sulphuric acid had the same properties as ethylic alcohol produced by fermentation (compare this vol., i, 182).   G. T. M.

Manufacture of Ethylic Alcohol from Sawdust. By E. SIMONSEN (*Bied.-Centr.*, 1899, **28**, 200—202; from *Festschr. tech. Schule Christiana*, 1898, 22. Compare Abstr., 1896, i, 331).—Sawdust and dilute acid are heated in an autoclave of 1 cubic metre capacity under a pressure of 9 atmospheres. The fineness or otherwise of the sawdust has no appreciable effect, and probably shavings, cut short, would answer equally well for the production of alcohol. The amount of liquid must be four times that of the wood, and it should contain 0·5 per cent. of sulphuric acid.

The extracted wood is pressed (17·1 kilograms per square centimetre) and afterwards used for burning.

As regards the amount of sugar produced, the usual quantity is about 22 per cent. of the air-dried wood. The volume of the solution varies, but is greater than that of the liquid added to the wood ; it contains about 5 per cent. of sugar. The acidity of the solution increases during the boiling ; the acid produced is, in part, acetic acid. It is not found desirable to use the same acid for more than one quantity of wood. In fermentation, the liquid is nearly, but not quite, neutralised ; the best temperature is 25° ; more than 75 per cent. of the sugar, determined with Fehling's solution, remained unfermented.

The greatest yield of alcohol amounted to 7 litres from 100 kilograms of air-dried sawdust ; the alcohol was of very good quality, and after being distilled over lime was as pure as rectified alcohol.

                    N. H. J. M.

Action of Fermentation Amylic Alcohol on Sodium Amyloxide. By GUERBET (*Compt. rend.*, 1899, **128**, 511—513).—When

sodium is dissolved in boiling fermentation amylic alcohol, consisting chiefly of the inactive modification, the products, in addition to hydrogen and sodium amyloxide, are sodium isovalerate, diamylic alcohol, $C_{10}H_{21} \cdot OH$, the isovalerate derived from this alcohol, and a *divaleric acid*, $C_{10}H_{20}O_2$.

Diamylic alcohol boils at 210—211° (corr.), and does not freeze at −20°, is a colourless liquid with a faint odour, dissolves in alcohol or ether, but is insoluble in water. Its *isovalerate* boils at 173—175° under 80 mm. pressure. *Divaleric acid*, $C_{10}H_{20}O_2$, is a colourless oil, insoluble in water, but soluble in alcohol and ether; it boils at 164—165° under 46 mm. pressure, and forms crystallisable sodium, calcium, and barium salts. In the reaction under consideration, it is produced from the alcohol by the action of sodium hydroxide, $C_{10}H_{21} \cdot OH + NaOH = C_{10}H_{19}O_2Na + 2H_2$, or by oxidation with chromic mixture.

The action of sodium amyloxide on amylic alcohol is represented by the equation $C_5H_{11} \cdot ONa + C_5H_{11} \cdot OH = C_{10}H_{21} \cdot OH + NaOH$, and the sodium hydroxide acts on some of the amylic alcohol and produces sodium isovalerate, and also acts on the higher alcohol in a similar manner. C. H. B.

Action of Alcohols on their Sodium Derivatives. By GUERBET (*Compt. rend.*, 1899, **128**, 1002—1004).—Diamylic alcohol (preceding abstract) has a sp. gr. 0·8491 at 0°; when heated with potassium hydrogen sulphate, it loses water and forms a liquid *decylene*, $C_{10}H_{20}$, of sp. gr. 0·7705 at 0°, boiling at 155°, and having an odour like turpentine. The *chloride*, $C_{10}H_{21}Cl$, obtained by the action of phosphorus pentachloride on the alcohol, is a colourless, oily liquid boiling at 130—132° under 70 mm. pressure; it cannot be distilled under ordinary pressure. *Diamylic acetate*, prepared by the action of acetic chloride on the alcohol, boils at 132—133° (corr.) under a pressure of 50 mm. and at 218—220° under atmospheric pressure, and has a sp. gr. 0·8701 at 0°. Diamylic isovalerate (*loc. cit.*) boils at 258—259° under atmospheric pressure. Divaleric acid (*loc. cit.*) is formed by the oxidation of diamylic alcohol with fused potash or chromic acid mixture; it is a colourless, oily liquid boiling at 162—163° and 248—250° under pressures of 50 and 760 mm. respectively. The *chloride*, $C_{10}H_{19}ClO$, boils at 115° under 60 mm. pressure, and the *amide*, $C_{10}H_{21}NO$, melts at 112°; the latter dissolves readily in alcohol, and is sparingly soluble in water.

When ethylic alcohol is heated with sodium ethoxide in sealed tubes at 210°, the following reaction occurs: $C_2H_6O + C_2H_5NaO = C_2H_4 + H_2 + CH_3 \cdot COONa$. Isobutylic alcohol, under these conditions, gives rise to a small quantity of sodium isobutyrate and another product boiling at 115—150°, which was not further characterised. G. T. M.

Oxidation of Secondary and Tertiary Amines. By WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1898, **128**, 682—683. Compare this vol., i, 243 and 244).—Trimethylamine hydrochloride and pyridine are not affected by potassium dichromate and sulphuric acid. Dimethylamine hydrochloride and α- and β-picolines are slightly oxidised, whilst β-lutidine, α- and β-collidines, quinoline, and lepidine are readily

decomposed, especially on warming the mixture. Azobenzene, under similar conditions, yields carbonic anhydride and a trace of nitrogen.

G. T. M.

Action of Nitrosyl Chloride on Fatty Amines. I. Primary Monamines. II. Secondary Amines. By WASSILY A. SOLONINA (*Chem. Centr.*, 1898, ii, 887—888; from *J. Russ. Chem. Soc.*, 30, 431—449, 449—453).—(1) When a solution of nitrosyl chloride in ether is slowly added to an ethereal solution of benzylamine at −15 to 20°, − benzylic chloride and benzylamine hydrochloride are formed. With isobutylamine, dissolved in metaxylene, under similar conditions, isobutylic chloride, with some tertiary butylic chloride and nitrosodi-isobutylamine, are formed, whilst pseudobutylamine yields pseudobutylic chloride, isoamylamine, and isoamylic chloride. Propylamine and ethylamine in ethereal solution yield propylic chloride and nitrosodiethylamine respectively, and from heptylamine, heptylic chloride and traces of heptylene are obtained. From the products of the reactions with allylamine and methylbutylallylcarbinamine, no definite compounds could be isolated. α-Camphylamine gives a good yield of α-camphylic chloride; this compound combines readily with bromine, and by the action of sodium phenoxide forms α-camphylic phenylic ether, $C_{10}H_{17}\cdot OPh$, which is easily soluble in alcohol, ether, and benzene, has a characteristic odour, and boils at 178—180° under 20 mm. pressure.

In the action of nitrosyl chloride on amines, the nitrous and hydrochloric acids resulting from the action of water on the chloride combine with the amines, and, probably, intermediate diazo-compounds are also formed. The formation of small quantities of isomerides was observed only in the cases of iso- and pseudo-butylamine.

(2) By the action of nitrosyl chloride on secondary amines, the hydrochlorides of the amines and nitrosamines are formed. In this way, nitrosodi-isobutylamine, nitrosodipropylamine, and nitrosodi-isoamylamine were obtained from the corresponding amines, and nitrosopiperidine from piperidine. The hydrochlorides of the amines were identified amongst the compounds obtained by means of benzenesulphonic chloride.

E. W. W.

Constitutional Formula of Hexamethylenetetramine. By GIUSEPPE GRASSI-CRISTALDI and A. MOTTA (*Gazzetta*, 1899, 29, i, 33—48).—The various constitutions which have been proposed for hexamethylenetetramine are discussed, and the conclusion drawn that the only one agreeing with all the known reactions is Lösekann's, namely, $N(CH_2\cdot N:CH_2)_3$. This formula brings out especially, firstly, the difference of one of the nitrogen atoms from the other three, as shown by the formation of only one hydrochloride, &c., by hexamethylenetetramine; and, secondly, its behaviour as a tertiary amine; it also serves to explain the formation of the dinitrosopentamethylenetetramine obtained by Griess and Harrow (Abstr., 1888, 1268). The authors are of opinion that the study of the aliphatic amines obtained by submitting the tetramine to the action of acids is of no value in deducing its constitution, as the first products would be ammonia and formaldehyde, which have been shown by Plöchl

(Abstr., 1888, 1051) to react, forming amines. They find on reducing hexamethylenetetramine in acid solution by means of zinc dust that Plöchl's reaction does not take place, as carbonic anhydride is not evolved; further, that mono- and tri-methylamine, instead of dimethyl-amine, are formed.　　　　　　　　　　　　　　　　　　T. H. P.

Methylpropylketoxime and Secondary Amylamine. By NICOLAI KURSANOFF (*Chem. Centr.*, 1898, ii, 473—474; from *J. Russ. Chem. Soc.*, 1898, **30**, 269—272).—*Methylpropylketoxime* boils at 168° under 748 mm. pressure, has a sp. gr. 0·92369 at 0° and 0·90711 at 20°, and when reduced in alcoholic solution with sodium, yields *secondary amylamine*, $NH_2 \cdot CHMe \cdot CH_2 \cdot CH_2Me$, which boils at 90° under 756 mm. pressure, and has a sp. gr. 0·75449 at 0° and 0·73839 at 20°. The hydrochloride, hydrobromide, nitrate, sulphate, platino-chloride, and aurichloride of the latter compound were prepared.

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Hexa-alkylated Diarsonium Compounds. By ALFRED PAR-THEIL, E. AMORT, and A. GRONOVER (*Arch. Pharm.*, 1899, **237**, 127—148).—When an aliphatic iodide is heated with arsenic mer-curide [prepared freshly (see this vol., ii, 417) and dried under diminished pressure] at 120°, or occasionally at 180°, the product is a yellow diarsonium mercuriodide, $As_2R_6I_2,2HgI_2$; this can be washed with ether and crystallised from alcohol. Methylic, ethylic, propylic, isopropylic, butylic, and allylic iodides react in this manner; so also benzylic iodide, but not phenylic iodide. By treatment with freshly precipitated silver chloride, the mercuriodide is converted into the compound $As_2R_6I_2,2HgCl_2$. With moist silver oxide, it yields the corresponding base, $As_2R_6(OH)_2$; this was not isolated; it forms an alkaline solution which absorbs carbonic anhydride, and by neutralis-ing this solution with the respective acids, the chloride, iodide, oxalate, &c., can be prepared, and from the chloride, the mercurichloride, platinochloride, and aurichloride may be obtained.

In the case of the propylic compounds, the crude base, hexapropyl-diarsonium hydroxide, $As_2Pr_6(OH)_2$, left on evaporation of the alco-holic solution, was distilled in a current of hydrogen in an oil-bath at 240°; the distillate contained tripropylarsine oxide, which was isolated by means of its compound with mercuric chloride, together with a substance of pronounced reducing power, doubtless dipropylarsine. Presumably, the decomposition took place according to the equation, $As_2Pr_6(OH)_2 = AsPr_3O + AsHPr_2 + PrOH$; propylic alcohol could not be detected, however, probably owing to the small amount of it present. If the distillate is allowed to remain in the air, crystals of propylcaco-dylic acid, $AsPr_2O \cdot OH$, are obtained; these must be formed by oxidation of the dipropylarsine.

Allylic iodide reacts with arsenic mercuride when the two sub-stances are simply boiled together in an open vessel, and in this case an attempt was made to ascertain the nature of the reaction. It appears to take place according to the equation $As_2Hg_3 + 8C_3H_5I = As_2(C_3H_5)_6I_2,2HgI_2 + HgI_2 + (C_3H_5)_2$ (diallyl), but at the same time a part of the allylic iodide decomposes into allylene and hydrogen iodide.

The compounds prepared are enumerated below, with their melting points and colour; as a rule, they crystallise well. Hexapropyldiarsonium compounds: *mercuriodide*, $As_2Pr_6I_2,2HgI_2$, 120°, yellow; *mercuriodo-chloride*, $As_2Pr_6I_2,2HgCl_2$, 150°; *mercurichloride*, $As_2Pr_6Cl_2,2HgCl_2$, 169°; *platinochloride*, $As_2Pr_6Cl_2,PtCl_4$, 189°, yellow; $AsPr_3O,2HgCl_2$, 60—60·5°; *dipropylarsinic (propylcacodylic) acid*, $AsPr_2O·OH$, 123°. Hexamethyldiarsonium compounds: *mercuriodide*, $As_2Me_6I_2,2HgI_2$, 184°, yellow; *iodide*, 171°; *mercurichloride*, $As_2Me_6Cl_2,2HgCl_2$, 211°; *platinochloride*, unmelted at 260°, yellow. Hexethyldiarsonium compounds: *mercuriodide*, $As_2Et_6Cl_2,2HgI_2$, 112°; *iodide*, 162°; *mercuri-chloride*, $As_2Et_6Cl_2,2HgCl_2$, 162°; *platinochloride*, $As_2Et_6Cl_2,PtCl_4$, 237°, yellow. Hexisopropyldiarsonium compounds: *mercuriodide*, $As_2Pr_6I_2,2HgI_2$, 114°, yellow; *iodide*, 150°; *mercurichloride*, $As_2Pr_6Cl_2,2HgCl_2$, 171°; *platinochloride*, $As_2Pr_6Cl_2,2PtCl_4$, 211°, yellow. Hexa-(normal)butyldiarsonium compounds: *mercuriodide*, $As_2Bu_6I_2,2HgI_2$, 109°, yellow; *iodide*, 146°; *platinochloride*, $As_2Bu_6Cl_2,PtCl_4$, 147°, yellow. Hexallyldiarsonium compounds: *mercuriodide*, $As_2All_6I_2,2HgI_2$, 62·5—63°, yellow; $As_2All_6I_2,HgCl_2$, 72·5°. Hexabenzyldiarsonium compounds: *mercuriodide*,

$$As_2(CH_2Ph)_6I_2,2HgI_2,$$

163°, yellowish; *chloride*, $As_2(CH_2Ph)_6Cl_2$, 138—140° when crystal-lised with $1\frac{1}{2}$ mols. of chloroform, 141—142·5° when crystallised with $4H_2O$; *mercurichloride*, $As_2(CH_2Ph)_6Cl_2,2HgCl_2$, 175·5°; *platino-chloride*, $As_2(CH_2Ph)_6Cl_2,PtCl_4 + H_2O$, 196—198°; *aurichloride*, $As_2(CH_2Ph)_6Cl_2,2AuCl_3$, yellow. C. F. B.

Precipitation of Acetone with Mercuric Sulphate. By CARL OPPENHEIMER (*Ber.*, 1899, **32**, 986—988).—The precipitate produced by the action of mercuric sulphate on acetone was stated by Denigès (this vol., ii, 256) to have the composition $6HgSO_4,9HgO,4COMe_2$ when dried at 100°, and $2HgSO_4,3HgO,COMe_2$ when dried at 110°. It is here stated that the precipitate does not lose in weight to any appreciable extent when heated at 110°, and its composition is intermediate between those corresponding with the two formulæ of Denigès. For the estimation of acetone, the factor 0·052 gives better results than the factor 0·06 deduced from the formula assigned to the precipitate. T. M. L.

Nitracetone. By LOUIS HENRY (*Ber.*, 1899, **32**, 865—867. Compare Lucas, this vol., i, 433).—Nitroisopropylic alcohol has no perceptible odour; it boils at 200—201° under 768 mm. pressure, dissolves in water, and readily yields the acetyl derivative with acetic chloride. Nitracetone has a penetrating odour, is insoluble in water, boils at 152° under 767 mm. pressure, and is indifferent towards acetic chloride. It combines with sodium ethoxide, yielding the *compound*, $C_3H_4NO_3Na$, produces a crystalline derivative with piperidino-methylic alcohol, and also acts vigorously on phenylhydrazine.

M. O. F.

Acetone Oils. By A. BUISINE and P. BUISINE (*Compt. rend.*, 1899, **128**, 561—562).—For the technical examination of acetone oils,

the authors determine the sp. gr., the solubility in water, the solubility in sodium hydrogen sulphite solution of 30° B., and the volume of the liquid that distils between different intervals of temperature. Acetone oil, from suint, of sp. gr. 0·830 to 0·835 at 15°, contains less than 5 per cent. of ordinary acetone, but at least 90 per cent. of ketones, 75 per cent. of which are soluble in water and consist mainly of methyl ethyl ketone.

Acetone oil of sp. gr. 0·842 from calcium pyrolignate contains a much smaller quantity of ketones boiling below 90°, and a much larger quantity of ketones boiling above 100°. C. H. B.

Acetone Oil from Calcium Pyrolignate as a Source of Methyl Propyl Ketone. By A. BUISINE and P. BUISINE (*Compt. rend.*, 1899, **128**, 885—887. Compare Abstr., 1898, i, 175, 352).—Calcium pyrolignate contains, besides calcium acetate, small quantities of the corresponding salts of the homologues of acetic acid ; in consequence of this, crude acetone, on rectification, yields about 5 per cent. of an oil distilling above 70°. From 44—68 per cent. of this " acetone oil " is insoluble in water, but only 6—8 per cent. is insoluble in sodium hydrogen sulphite ; it consists largely of methyl propyl ketone and methyl isopropyl ketone, the normal isomeride predominating ; traces of methyl ethyl ketone are also present. In order to separate the principal constituents, the oil is treated with excess of a concentrated solution of sodium hydrogen sulphite ; the precipitate produced is decomposed with warm sodium carbonate solution and the oil which results is dried over potassium carbonate and fractionated. The constituents of the mixture are identified by means of their semi-carbazides. One sample of acetone oil treated in this way yielded 45 per cent. of the two isomerides. G. T. M.

Amidodiethyl Ketone and Amidodiethylcarbinol. By ERNST JÄNECKE (*Ber.*, 1899, **32**, 1095—1103).—*Amidodiethyl ketone,* $NH_2 \cdot CHMe \cdot COEt$, is obtained by reducing isonitrosodiethyl ketone (Claisen and Manasse, Abstr., 1889, 585) with stannous chloride and hydrochloric acid ; the deliquescent *hydrochloride,* and the yellow *picrate* and *platinochloride* melt at 128°, 132°, and 154° respectively. The base itself cannot be isolated, diethyldimethylpyrazine being obtained instead. When the hydrochloride is warmed with potassium thiocyanate, a methylethylimidazolyl-μ-mercaptan is obtained, and when this is oxidised with warm dilute nitric acid or boiled with ethylic nitrite in alcoholic solution, it yields a methylethylimidazole (ethylmethyl-glyoxaline). These substances appear to be identical with those previously obtained from methyl amidopropyl ketone, $NH_2 \cdot CHEt \cdot COMe$ (Gabriel and Posner, Abstr., 1894, i, 355), and hence each must be capable of existing in two tautomeric forms.

$$CX \!\!\begin{array}{c} NH \cdot CMe \\ \mid\mid \\ N \!\!-\!\! CEt \end{array} \quad \text{and} \quad CX \!\!\begin{array}{c} N \!\!-\!\! CMe \\ \mid\mid \\ NH \cdot CEt \end{array} \quad [X = SH \text{ or } H].$$
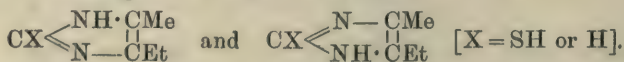
With potassium cyanate in aqueous solution, the hydrochloride of

amidodiethyl ketone yields a methylethylimidazolone, $\begin{matrix} CMe \cdot NH \\ CEt \cdot NH \end{matrix} > CO$,

identical with that obtained from methyl amidopropyl ketone (*loc. cit.*).

When methylethylglyoxime, $NOH\!:\!CMe\cdot CEt\!:\!NOH$ (Claisen and Manasse, *loc. cit.*), is reduced with stannous chloride and hydrochloric acid, it does not yield the diamine, $NH_2\cdot CHMe\cdot CHEt\cdot NH_2$, but a mixture of the hydrochlorides of methyl amidopropyl and of amidodiethyl ketones.

Amidodiethylcarbinol, $NH_2\cdot CHMe\cdot CHEt\cdot OH$, is obtained when the hydrochloride of amidodiethyl ketone is reduced in ice cold aqueous solution by adding normal hydrochloric acid and $2\frac{1}{2}$ per cent. sodium amalgam in successive small portions until the solution no longer reduces Fehling's solution. It is obtained in better yield, however, when isonitrodiethyl ketone is reduced in the same manner. It boils at 169—173°, and has a sp. gr. 0·9289 at 23·5°; the yellow *platinochloride* melts at 154°. With phenylthiocarbimide, it unites, forming *phenylhydroxyamylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot CHMe\cdot CHEt\cdot OH$; this melts at 96° and when heated with strong hydrochloric acid for 6 hours at 100°, yields yellowish-brown *μ-phenylpentylene-ψ-thio-carbamide*, $NPh\!:\!C\begin{matrix} NH\cdot CHMe \\ S\text{---}CHEt \end{matrix}$; this melts at 129°, and its yellow *picrate* at 189°. The analogous *ethyl* derivatives were prepared by using ethyl-, instead of phenyl-thiocarbimide; the thiocarbamide melts at 104—105°; the ψ-thiocarbamide is an oil, but its *picrate* melts at 123°. When the carbinol is heated with concentrated hydrobromic acid at 100°, it forms 3-*bromo*-2-*amidopentane*, $NH_2\cdot CHMe\cdot CHEtBr$; the *hydrobromide* of this melts at 139°, the yellow *picrate* at 165°. With benzoic chloride and dilute caustic potash, the solution being shaken and cooled, the hydrobromide yields *μ-phenyl-β-methyl-a-ethyl-oxazoline*, $CPh\begin{matrix} N\cdot CHMe \\ O\cdot CHEt \end{matrix}$, which boils at 160—162° under a pressure of 35—37 mm., decomposing to some extent, and forms a yellow *picrate* melting at 138°; with carbon bisulphide and caustic potash in cooled aqueous alcoholic solution, it yields *μ-mercapto-β-methyl-a-ethyl-thiazoline*, $SH\cdot C\begin{matrix} N\cdot CHMe \\ S\cdot CHEt \end{matrix}$, which melts at about 70°.　C. F. B.

The Silver Salts of *d*-, *l*-, **and** *dl*-**Methylethylacetic Acid and the Synthesis of** *d*-**Valeric Acid.** By WILHELM MARCKWALD (*Ber.*, 1899, **32**, 1089—1094).—Küster (Abstr., ii, 549) has made certain assumptions in the calculation which leads him to conclude that inactive silver valerate exists in solution as a racemic compound. These assumptions are not altogether justifiable, and his conclusion is invalidated thereby.

In this connection, the solubility of inactive silver valerate (methylethylacetate) has been redetermined, and found to be considerably less than has been stated hitherto. Either excess of the salt was shaken with water for six hours, or a hot, saturated solution was cooled, and then shaken for six hours with the salt that had separated out. The solution was then filtered, and titrated with $N/20$ ammonium thiocyanate; it was first made acid with sulphuric acid, as ferric valerate is insoluble in

neutral solution; 100 c.c. of the saturated solution contain, at 16°, 0·880, at 20°, 0·940 gram of the salt. When water is shaken with excess of both the inactive and the *l*-salt, or when a saturated solution of the *l*-salt is shaken with excess of the inactive salt, the resulting solution is found in both cases to contain the above amount of salt per 100 c.c., and to be optically inactive, whereas the undissolved solid yields an active solution. It must follow from this that the inactive silver salt is merely a conglomerate of the *d*- and *l*-forms, and not a racemic compound; otherwise, the solution would have been lævorotatory in both cases, and would have contained an amount of silver salt corresponding to the sum of the solubilities of the inactive and *l*-salts.

Advantage may be taken of these facts to obtain synthetical *d*-valeric acid in a pure state. The impure acid with $a_D = +10°$ in a 100 mm. tube (Abstr., 1896, i, 203), containing about 80 per cent. of the *d*-acid, was converted into the silver salt, enough water being used to keep all the *l*-salt along with an equal amount of *d*-salt in solution. The *d*-silver salt which crystallised out was recrystallised from water and converted into the acid; this boiled constantly at 174°, and had the rotation $a_D = +8° 10'$ in a 5 cm. tube at the ordinary temperature; the solubility of the silver salt is 0·680 gram per 100 c.c. at 16°, and 0·730 at 20°. This acid is identical with that obtained by Taverne (Abstr., 1895, i, 119) by hydrolysing convolvulin; the solubility of the silver salt prepared from a sample of Taverne's acid was 0·732 gram per 100 c.c. (compare also Abstr., 1896, i, 203—204, for solubilities of the *l* and inactive *dl* salt). C. F. B.

Rancidity of Fats. By ALBERTO SCALA (*Bied. Centr.*, 1899, **28**, 196—198; from *Staz. sper. agrar. ital.*, 1897, 613).—Olive oil, pig's fat, and butter, when rancid, showed greatly diminished iodine numbers, and contained less non-volatile fatty acids than when fresh, whilst the refractive index, the volatile fatty acids, and the ether numbers increased.

Further experiments with olive oil, pig's fat, and tallow showed that, when exposed to air and light, olive oil gained 9 per cent., pig's fat 3·5 per cent., whilst tallow (with an iodine number of only 25) gained only 1·5 per cent., oleic acid gained 8·35 per cent., whilst stearic and palmitic acids lost slightly in weight.

It is therefore concluded that rancidity depends alone on the oxidation of oleic and other acids of that series. Very rancid olive oil yielded œnanthaldehyde when distilled with steam. Hydrolysis produced formic, acetic, butyric, and œnanthic acids; also some non-volatile acids, $C_nH_{2n-2}O_n$, including azelaic and sebacic acids.

In rancid oleic acid, the same compounds were detected, and, in addition, a solid substance (dihydroxystearic acid) which causes opacity and viscosity. The increase of density observed in rancid fats is partly due to the production of solids. N. H. J. M.

Two Modifications of Ethylic β-Amidocrotonate. By EMIL KNOEVENAGEL (*Ber.*, 1899, **32**, 853—857. Compare Behrend, this vol., i, 331).—The two forms of ethylic β-amidocrotonate described by Behrend (*loc. cit.*) have been also obtained by the author, and solidify at 23—24° and 34° respectively. Both forms have a sp. gr. 1·0144

at 36°, and the refractive index is also the same in each case; the behaviour of each form towards ethylic benzylideneacetoacetate (compare Abstr., 1898, i, 447) is also identical, and on these grounds the author regards the two modifications as physical isomerides.

M. O. F.

Isomeride of Hydroxymenthylic Acid. By GEORGES LÉSER (*Compt. rend.*, 1899, 128, 734—736).—When acetylmethylheptenone is mixed at the ordinary temperature with six times its weight of 80 per cent. sulphuric acid, it is mainly converted into a mixture of two compounds, $C_{10}H_{16}O_2$ and $C_{10}H_{14}O$, which boil at 125—135° under 20 mm. pressure and are soluble in ether. The mixture gives the β-diketone reaction with ferric chloride, and when treated with potassium methoxide in excess of methylic alcohol, yields an oily liquid volatile in steam and the potassium salt of an acid, $C_{10}H_{18}O_3$. This acid boils at 190—191° under 20 mm. pressure, and melts at 98°; it forms a deliquescent barium salt and a crystallisable silver salt soluble in water and stable when exposed to light. The ethylic salt boils at 149° under 20 mm. pressure and has a strong, fruity odour; the oxime crystallises from dilute alcohol in small, brilliant prisms which melt at 98°. The acid is isomeric with Arth's hydroxymenthylic acid and with Baeyer's isopropylheptanonoic acid; most probably it is isopropyl-4-heptanone-6-oic acid.

C. H. B.

Solubility of the Normal Acids of the Oxalic Series. By F. LAMOUROUX (*Compt. rend.*, 1899, 128, 998—1000).—Henry (Abstr., 1885, 335) stated that the dibasic acids of the oxalic series containing an even number of carbon atoms are slightly soluble in water, whilst those containing an odd number of carbon atoms are readily soluble. In the case of the second group, the solubility of the three initial members only had been determined. The author finds that the third member, pimelic acid, is in reality very slightly soluble, and that the succeeding members, azelaic and brassylic acids, are as insoluble as their homologues containing an even number of carbon atoms. A table is given showing the solubility of these dibasic acids through a range of temperature from 0° to 66°, and it is shown that, in general, these acids are very insoluble in water, but that to this rule there are two exceptions, as malonic and glutaric acids readily dissolve in this solvent.

G. T. M.

Solubility of Substituted Malonic Acids. By GUSTAVE MASSOL and F. LAMOUROUX (*Compt. rend.*, 1899, 128, 1000—1002. Compare preceding abstract).—Determinations of the solubilities of a series of monosubstituted malonic acids show that they are all very soluble in water, and that the introduction of an alkyl radicle diminishes the solubility of malonic acid; in the case of succinic acid, the introduction of alkyl groups increases the solubility. Those substituted malonic acids containing an odd number of carbon atoms are more soluble than those containing an even number, but the difference becomes very small when the temperature is raised. When compared with the normal dibasic acids containing the same number of carbon atoms, the derivatives of malonic acid are found to be

far more soluble. These results indicate that it is not possible
at present to deduce any conclusions as to the relationship between
the solubility of the dibasic acids and their molecular structure.

<div align="right">G. T. M.</div>

**Separation of the Dibasic Acids formed by the Oxidation
of Fats.** By Louis Bouveault (*Bull. Soc. Chim.*, 1898, [iii], **19**,
562—565).—The statement of Aerppe (*Bull. Soc. Chim.*, 1866, [ii],
5, 59), that pimelic acid is not formed by the oxidation of fats, has
hitherto been generally accepted, but it is now shown that all the
normal dibasic acids of the oxalic series, from su ccinic acid to sebacic
acid, are thus produced. The process recommended for their separa-
tion comprises the following operations :—1. Heating under the
ordinary pressure, until a temperature of 230° is reached, whereby
the whole of the succinic acid is converted into succinic anhydride, a
portion of which distils over.   2. Distillation under diminished
pressure to complete the separation of succinic anhydride.   3. Treat-
ment of the residue with ether, which leaves undissolved a mixture of
pimelic and adipic acids.   4. Crystallisation of this mixture from
water, whereby pure adipic acid is obtained, whilst pimelic acid
remains in solution.   5. Conversion of the acids contained in the
ethereal extract and the aqueous mother liquors into their calcium
salts   Calcium glutarate, being very soluble in water, is easily
separated from calcium pimelate, which is slightly soluble in cold,
but insoluble in boiling, water.   N. L.

αα-**Dimethylglutaric Acid.** By Edmond E. Blaise (*Compt. rend.*,
1899, **128**, 676—678. Compare Abstr., 1898, i, 561, 631).—Cyano-
dimethylsuccinic acid, obtained by hydrolysing its ethereal salt
(compare Abstr., 1894, i, 492), loses carbonic anhydride when heated
at 123° ; this decomposition does not give rise to cyanodimethyl-
propionic acid, but to its isomeride, dimethylsuccinimide. The *ethylic*
salt of cyanodimethylpropionic acid, $CN \cdot CH_2 \cdot CMe_2 \cdot COOEt$, pro-
duced by heating the monethylic salt of cyanodimethylsuccinic acid,
boils without decomposition at 217—220° under atmospheric
pressure. The *hydrochloride* of ethylic γ-amido-α-dimethylbutyrate,
$COOEt \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot NH_2, HCl$, obtained by reducing the pre-
ceding compound with sodium and absolute alcohol and subsequently
treating the product with hydrochloric acid, crystallises in needles
melting at 112°. The corresponding *hydrobromide* and *sulphate* melt
at 142° and 145° respectively.

These derivatives may also be obtained by starting from *αα*-dimethyl-
glutaric acid. The anhydride of this acid, when mixed with alcoholic
ammonia, yields ammonium *αα*-dimethylglutaramate ; the corre-
sponding sodium salt, when treated in succession with alkaline hypo-
bromite and alcoholic hydrogen bromide, gives rise to the hydro-
bromide melting at 142° ; from this salt, the hydrochloride and
sulphate may be obtained. On attempting to liberate γ-amido-
α-dimethylbutyric acid from any one of these salts, 3 : 3-*dimethyl-
pyrrolidone* is produced ; this substance crystallises in nacreous
leaflets, melts at 65—67°, and boils without decomposition at 237°
under atmospheric pressure.   G. T. M.

Formation of Olefindicarboxylic Acids from Ethylic Dibromomonalkylacetoacetates. By MAX CONRAD (*Ber.*, 1899, **32**, 1005—1008).—The author explains the formation of mesaconic acid from ethylic γ-dibromo-α-methylacetoacetate thus: $CHBr_2 \cdot C(OH){:}CMe \cdot COOEt \longrightarrow CH(OH)_2 \cdot C(OH){:}CMe \cdot COOH \longrightarrow C(OH)_2{:}C{:}CMe \cdot COOH \longrightarrow COOH \cdot CH{:}CMe \cdot COOH$ (compare Wolff, Abstr., 1891, 417, and Cloez, Abstr., 1890, 739). An analogous change occurs in the case of the αα-dihalogen β-ketones (Faworsky, Abstr., 1894, i, 391), which are converted into unsaturated monobasic acids. It is now shown that unsaturated tribasic acids can be produced in a similar way, for instance, ethylic dibromoacetylsuccinate has been converted into aconitic acid, $CHBr_2 \cdot CO \cdot CH(COOEt) \cdot CH_2 \cdot COOEt \longrightarrow COOH \cdot CH{:}C(COOH) \cdot CH_2 \cdot COOH$, by the action of baryta water.

T. M. L.

Action of Ethylic Sodiomalonate on the Dibromides, $C_nH_{2n}Br_2$. By WLADIMIR IPATIEFF (*Chem. Centr.*, 1898, ii, 660—661; from *J. Russ. Chem. Soc.*, 1898, **30**, 391—400).—*Ethylic dimethylallylmalonate*, $CMe_2{:}CH \cdot CH_2 \cdot CH(COOEt)_2$, formed by slowly adding sodium dissolved in absolute alcohol to a mixture of dibromo-β-dimethyltrimethylene and ethylic malonate, is an oil with a pleasant odour, boils at 140—141° under 20 mm. pressure, and decolorises potassium permanganate. The *oxime* crystallises from benzene in colourless prisms and melts at 85—87°. The *acid* melts at 82·5—83·5°, is soluble in water, alcohol, and ether, quickly decolorises potassium permanganate, and when heated above the melting point loses carbonic anhydride and forms a monobasic, unsaturated acid. The calcium, sodium, and ammonium salts are easily soluble in water, but the salts of the heavy metals are insoluble. The silver salt, obtained by precipitating a solution of the ammonium salt with silver nitrate, is a white, crystalline precipitate.

By the action of ethylic sodiomalonate on dibromotrimethylethylene, trimethylethylene and ethylic ethanetetracarboxylate are formed. Dibromisobutylene acts on ethylic sodiomalonate in a similar manner; hence, generally, all dibromides containing one bromine atom united to a tertiary and the other to a primary or secondary carbon atom react with ethylic sodiomalonate forming olefines and ethylic ethanetetracarboxylate.

E. W. W.

Preparation and Properties of β-Hydroxy-αα₁-dimethylglutaric Acid. By SERGIUS N. REFORMATSKY (*Chem. Centr.*, 1898, ii, 885—886; from *J. Russ. Chem. Soc.*, **30**, 453—466).—By the action of zinc on a mixture of ethylic bromopropionate and ethylic formate, a compound, $ZnBr \cdot O \cdot CH(CHMe \cdot COOEt)_2$, is formed, which, when treated with water, yields ethylic β-hydroxy-αα₁-dimethylglutarate. By using a copper–zinc couple, a yield of 88·6 per cent. of the ethylic salt may be obtained. The corresponding *acid* crystallises best from ethylic acetate, melts at 136—137°, is easily soluble in water, ether, alcohol, glacial acetic acid, acetone, and ethylic formate, slightly in carbon bisulphide, benzene, and light petroleum, and has the electrical dissociation constant, $k = 0\cdot0122$ (Michailenko). The barium, sodium, potassium, and silver salts were prepared.

β-*Acetoxy-aa₁-dimethylglutaric anhydride*, $OAc \cdot CH \underset{CHMe \cdot CO}{\overset{CHMe \cdot CO}{<}} O$,

prepared by the action of acetic chloride on the acid, separates in large crystals, is easily soluble in benzene, and with cold water forms the corresponding *acid*, $OAc \cdot CH(CHMe \cdot COOH)_2$, which melts at 120—121°, is soluble in ether and chloroform, insoluble in light petroleum, has the electrical dissociation constant $k = 0.0200$, and forms a barium salt, $C_9H_{12}O_6Ba + 3H_2O$. The *monotoluidide* separates in a lustrous, silky mass, melts at 129—130°, and decomposes at 170° with liberation of gas. The acetyl group of the anhydride is only partially hydrolysed by alcoholic potassium hydroxide.

By the action of hydriodic acid on hydroxydimethylglutaric acid, in addition to the mixture of fumaroid and maleoid aa_1-dimethylglutaric acids which Auwers obtained, aa_1-dimethylglutaconic acid, $COOH \cdot CHMe \cdot CH \colon CMe \cdot COOH$, was also formed in one experiment. This acid, which is better prepared by the action of an 80 per cent. solution of hydriodic acid on the ethylic salt or by oxidising the acid with sulphuric acid, crystallises in lustrous needles, melts at 147°, and is easily soluble in hot water, but only slightly so in cold.

Ethylic β-hydroxy-aa_1-dimethylglutarate, when hydrolysed, yields, not only the crystalline acid, but also an acid with similar properties which separates as a syrup and is probably an isomeride ; the latter acid, when heated with hydriodic acid, forms the dimethylglutaconic acid with the lower melting point, whilst by the action of sulphuric acid it yields the acid which melts at 147°. By the action of acetic chloride, it forms a compound which crystallises in slender needles, melts at 132.5° and is probably the acetoxyanhydride, since with water it gives the corresponding acid which separates in large crystals, melts at 82.5—83.5° and yields a barium salt, $C_9H_{12}O_6Ba + 2H_2O$. The paratoluidide, $C_{16}H_{21}NO_5$, prepared from the anhydride melts at 181.5—182°.   E. W. W.

Action of Zinc on a Mixture of Ethylic Bromisobutyrate and Ethylic Formate. Synthesis of Symmetrical β-Hydroxytetramethylglutaric Acid. By JACKOV. I. MICHAILENKO (*Chem. Centr.*, 1898, ii, 885 ; from *J. Russ. Chem. Soc.*, 30, 466—475).— Ethylic β-hydroxytetramethylglutarate, prepared by the action of zinc on a mixture of ethylic bromisobutyrate and ethylic formate, decomposes on distillation ; hence, the portion boiling below 200° was distilled off and the residue hydrolysed. The acid, $OH \cdot CH(CMe_2 \cdot COOH)_2$, crystallises in short prisms, melts and decomposes at 162—165°, is soluble in water, alcohol, ether, and ethylic acetate, and has the electrical dissociation constant $k = 0.0133$. The *potassium, sodium, barium, calcium, lead*, and *silver* salts were prepared.

β-*Acetoxytetramethylglutaric anhydride*, $OAc \cdot CH \underset{CMe_2 \cdot CO}{\overset{CMe_2 \cdot CO}{<}} O$,

obtained by the action of acetic chloride on hydroxytetramethylglutaric acid, melts at 88—89°, and when treated with water, yields the acid which crystallises in four-sided leaflets, melts at 158—159° and has the electrical dissociation constant $k = 0.005166$. The *potassium, barium*, and *silver* salts are described. The *paratoluidide*, prepared by the

action of paratoluidine on the anhydride, separates in slender, hair-like crystals and melts at 157—159°. E. W. W.

Racemic Transformation of Potassium Racemate. By JACOBUS H. VAN'T HOFF and WOLF MÜLLER (*Ber.*, 1899, **32**, 857—859. Compare Roozeboom, this vol., ii, 276).—Potassium racemate crystallises with $1H_2O$ (rhombic) and with $2H_2O$ (mono-clinic); both forms lose water when heated, the monohydrate under-going this change at 30°. The dihydrate undergoes transformation into the active components at 71·78°, in accordance with the equation

$$2C_4H_4O_6K_2, 2H_2O = (\overset{\rightarrow}{}C_4H_4O_6K_2, \tfrac{1}{2}H_2O + \overset{\leftarrow}{})C_4H_4O_6K_2, \tfrac{1}{2}H_2O + 3H_2O.$$

This behaviour resembles that of hydrogen ammonium malate (Kenrick, Abstr., 1897, i, 506). M. O. F.

Parapyruvic Acid. By LUDWIG WOLFF (*Annalen*, 1899, **305**, 154—165).—Finck observed that pyruvic acid, when treated with excess of baryta, yields a sparingly soluble basic salt which gives rise to uvitic acid under the influence of the boiling agent; carbonic anhydride converts the salt into a readily soluble normal derivative. Aqueous solutions of the pyruvates undergo slow spontaneous trans-formation into the salts of so-called syrupy pyruvic acid, the action being hastened by small quantities of such condensing agents as potassium cyanide, caustic potash, baryta, and ammonia; the salts ob-tained in this way are normal derivatives of the dibasic acid, $C_6H_8O_6$, but larger proportions of the condensing agent give rise to compounds allied to the basic salt obtained by Finck. The acid from which these salts are derived is termed *parapyruvic acid*; it probably has the con-stitution expressed by the formula, $COOH \cdot CMe(OH) \cdot CH_2 \cdot CO \cdot COOH$, and is unstable in the free condition, becoming in part converted into ketovalerolactonecarboxylic acid. Parapyruvic acid is regarded as the intermediate product in the synthesis of methyldihydrotrimesic acid from pyruvic acid, and this suggestion accounts for the difference in behaviour exhibited by acetone and pyruvic acid on condensation; it should be mentioned, however, that alkalis regenerate a small pro-portion of pyruvic acid from the para-acid.

Normal *barium* parapyruvate is a white, granular substance contain-ing $5\tfrac{1}{2}H_2O$; it is somewhat sparingly soluble in water and dilute acetic acid, but dissolves more readily in sodium acetate, and freely in hydrochloric acid, which converts it into the lactonic acid. Protracted treatment with dilute acetic acid gives rise to a modification which contains $4\tfrac{1}{2}H_2O$, and is probably identical with a salt obtained by Mulder from the basic barium salt and acetic acid. The *calcium* salt contains $4H_2O$. The *lead* salt is precipitated on mixing aqueous solutions of pyruvic acid and lead acetate, and crystallises in small plates.

When barium parapyruvate is decomposed with sulphuric acid, a mixture of 20 per cent. of parapyruvic acid with 80 per cent. of the lactonic acid is obtained; it forms a colourless, viscous syrup, which yields a clear solution in water, and gives no precipitate with phenyl-hydrazine hydrochloride. Hot concentrated sodium hydroxide converts the syrup into methyldihydrotrimesic and oxalic acids; cold alkalis

regenerate the salts of parapyruvic acid, whilst alkali carbonates yield salts of the lactonic acid. M. O. F.

Composition and Crystalline Form of Malates. By HERMANN TRAUBE (*Zeit. Kryst. Min.*, 1899, **31**, 160—178).—Crystallographic descriptions are given of the following salts of malic acid. The observations all agree with Pasteur's law of the enantiomorphism of crystals of optically active substances. The best method of preparing the salts is by the interaction of strontium hydrogen malate with the sulphate of the metal.

$KC_4H_5O_5 + 3\frac{1}{2}H_2O$,	Rhombic, hemihedral,	$0\cdot5355 : 1 : 0\cdot5471$
$RbC_4H_5O_5 + 3\frac{1}{2}H_2O$,	,,	$0\cdot4986 : 1 : 0\cdot5136$
$NH_4\cdot C_4H_5O_5$,	,,	$0\cdot723 \ : 1 : 0\cdot7726$
$NaC_4H_5O_5 + 2H_2O$,	,,	$? \ : 1 : 0\cdot9705$
$LiC_4H_5O_5 + H_2O$,	Tetragonal, trapezohedral,	$1 : 1\cdot2447$
$LiC_4H_5O_5 + 6H_2O$,	Monoclinic, hemimorphic,	$0\cdot3917 : 1 : 0\cdot4890 ; \ \beta = 41° \ 12'.$
$Li_2C_4H_4O_5 + H_2O$,	Rhombic,	$0\cdot6556 : 1 : 0\cdot7033$
$Ca(C_4H_5O_5)_2 + 6H_2O$,	Rhombic, hemihedral,	$0\cdot9418 : 1 : 1\cdot0556$
$Sr(C_4H_5O_5)_2 + 6H_2O$,	,,	$0\cdot9646 : 1 : 0\cdot9037$
$CaC_4H_4O_5 + 3H_2O$,	,,	$0\cdot4375 : 1 : 1\cdot0932$
$Mg(C_4H_5O_5)_2 + 2H_2O$,	Tetragonal, trapezohedral,	$1 : 2\cdot0536$
$Zn(C_4H_5O_5)_2 + 2H_2O$,	,,	$1 : 2\cdot0041$
$Cu(C_4H_5O_5)_2 + 2H_2O$,	,,	$1 : 1\cdot9953$
$Mn(C_4H_5O_5)_2 + 2H_2O$,	,,	$1 : 2\cdot0156$
$Co(C_4H_5O_5)_2 + 2H_2O$,	,,	$1 : 2\cdot0245$
$Ni(C_4H_5O_5)_2 + 2H_2O$,	,,	$1 : 1\cdot9963$
$Cu(C_4H_5O_5)_2 + H_2O$,	Monoclinic, hemimorphic,	$0\cdot7668 : 1 : 0\cdot9699 ; \ \beta = 86° \ 4'.$
$MgC_4H_4O_5 + 3H_2O$,	,,	$0\cdot8579 : 1 : 0\cdot6015 ; \ \beta = 74° \ 24'.$
$ZnC_4H_4O_5 + 3H_2O$,	,,	$0\cdot8619 : 1 : 0\cdot5762 ; \ \beta = 73° \ 42'.$
$MnC_4H_4O_5 + 3H_2O$,	,,	$0\cdot8871 : 1 : 0\cdot6692 ; \ \beta = 78° \ 30'.$
$CoC_4H_4O_5 + 3H_2O$,	,,	$0\cdot9197 : 1 : 0\cdot6386 ; \ \beta = 73° \ 0'.$
$MgC_4H_4O_5 + 5H_2O$,	Rhombic, hemihedral,	$0\cdot7378 : 1 : 0\cdot4040$
$MnC_4H_4O_5 + 4H_2O$,	,,	$0\cdot9844 : 1 : 1\cdot1076$

L. J. S.

New Method of Preparing Ethylic Dicarbintetracarboxylate [Ethylenetetracarboxylate]. By RUBIN BLANK and E. SAMSON (*Ber.*, 1899, **32**, 860. Compare Conrad and Brückner, Abstr., 1892, 39; also Bischoff, Abstr., 1896, i, 130).—When anhydrous potassium carbonate acts on a solution of ethylic bromomalonate in some indifferent solvent, hydrogen bromide is eliminated and ethylic ethylenetetracarboxylate, $C(COOEt)_2 : C(COOEt)_2$, produced. Ethylic chloromalonate behaves in the same way, but the action is less energetic. M. O. F.

Dithiobiurets. By EMIL FROMM and E. PHILIPPE (*Ber.*, 1899, **32**, 835—848).—*Ethylic a-phenyldithio-C-methylketuretcarboxylate* or *a-phenyl-*b : c- (*ethylic 2 : 2-butanecarboxylate*)-*dithiobiurimine*,

$$SH\cdot C\cdot N\cdot C(SH) : NPh$$
$$N\cdot C Me\cdot CH_2\cdot COOEt'$$
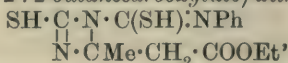
formed when hydrogen chloride is passed into a mixture of phenyl-thiobiuret and ethylic acetoacetate, separates from alcohol in colourless crystals, melts at 219—220°, and dissolves somewhat readily in glacial acetic acid, but only sparingly in water and alcohol; the corresponding *acid*, $C_{12}H_{13}N_3S_2O_2$, made by hydrolysing the ethereal salt with dilute alcoholic soda, crystallises in slender, white needles,

and melts at 214—216°; when shaken with benzylic chloride and dilute soda, it yields a *dibenzyl-benzylic* salt, $C_{33}H_{31}N_3S_2O_2$, which crystallises from alcohol in colourless needles and melts at 133°. When the acid is heated with acetic anhydride, it gives a mixed *anhydride*, $\begin{array}{c} CS-N\cdot CS\cdot NHPh \\ | \quad | \\ NH\cdot CMe\cdot CH_2\cdot COOAc \end{array}$, which becomes crystalline when the cooled product is left during 24 hours, but cannot be crystallised from acetic acid, as it decomposes very readily in presence of moisture; it may be purified by dissolution in cold acetone and precipitation with light petroleum, when it separates in colourless crystals melting at 168°.

Phenyl-methylimidothiazoline-thiocarbamide,

$$\begin{array}{c} CH:CMe \\ | \\ S\cdot C(NH) \end{array}\!\!>\!N\cdot C(SH):NPh \quad \text{or} \quad \begin{array}{c} CH\!-\!-\!S \\ || \\ CMe\cdot NH \end{array}\!\!>\!C:N\cdot C(SH):NPh,$$
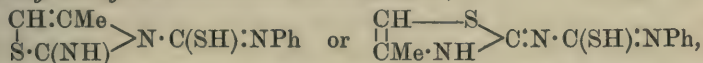
is obtained as the *hydrochloride*, $C_{11}H_{11}N_3S_2,HCl$, by warming phenyl-dithiobiuret with twice its weight of monochloracetone; this separates as a crystalline mass, and may be purified by crystallisation from alcohol, when it forms shining, white needles, melts at 163°, and is insoluble in ether, but dissolves sparingly in water and readily in alcohol; the *base* separates on spontaneous evaporation of its ethereal solution in light yellow crystals, and melts and decomposes at 163°. The *benzyl* derivative, $C_{18}H_{17}N_3S_2$, forms colourless crystals and melts at 89—90°.

Phenylmethyl-methylimidothiazoline-thiocarbamide,

$$\begin{array}{c} CH:CMe \\ | \\ S\cdot C(NH) \end{array}\!\!>\!N\cdot CS\cdot NPhMe \quad \text{or} \quad \begin{array}{c} CH\!-\!-\!S \\ || \\ CMe\cdot NH \end{array}\!\!>\!C:N\cdot CS\cdot NPhMe,$$
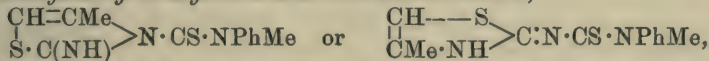
is obtained as the *hydrochloride*, $C_{12}H_{13}N_3S_2,HCl$, melting at 216°, when phenylmethyldithiobiuret is warmed with monochloracetone on a water-bath. The *base*, obtained by dissolving the salt in alcohol and precipitating with water, separates from ether in radiating crystals, melts at 84°, and is insoluble in water, but dissolves readily in alcohol and ether; it does not give a benzyl derivative on treatment with soda and benzylic chloride.

When phenyldithiobiuret is warmed with four times its weight of acetic anhydride, it dissolves, turns brown, and finally hydrogen sulphide is evolved; if, before the last stage, the liquid is poured into water, a mixture of crystalline substances is obtained, and on dissolving this in boiling alcohol and allowing to cool, *monacetyldithiobiuret*, $C_{10}H_{11}N_3S_2O$, separates, whilst the mother liquor yields the *diacetyl* compound, $C_{12}H_{13}N_3S_2O_2$; both crystallise in yellow needles, the former melting at 184° and the latter at 193°. A. L.

Mercury Substitution Derivatives of Alcohol and Acetic Acid. By KARL A. HOFMANN (*Ber.*, 1899, **32**, 870—880. Compare this vol., i, 97).—The *compound*, $C_2Hg_4Cl_4$, obtained by the action of mercuric chloride on absolute alcohol under the influence of sodium ethoxide or sodium acetate, forms a white powder resembling calomel; it immediately becomes black when treated with ammonia, potassium cyanide, or caustic alkalis, and yields mercury with a hot mixture of caustic soda and potassium cyanide, the odour of aldehyde resin

becoming perceptible. Hot alkalis convert the substance into a black residue and a colourless solution, from which hydrochloric acid precipitates trimercuracetic acid. A boiling solution of hydrazine hydrate eliminates all the mercury, and forms a compound of hydrazine and aldehyde, with liberation of 4·3 per cent. of nitrogen; in consequence of this result, the author ascribes to the mercury derivative a constitution expressed by the formula $Hg{<}^{CCl\cdot HgCl}_{C(HgCl)_2}$. When the substance is heated with mercuric oxide and caustic alkali at 105—110°, dimercuracetic and trimercuracetic acids are produced, along with the explosive base, $C_2Hg_6O_4H_2$ (Abstr., 1898, i, 635).

The *compound*, $C_2Hg_3Cl_4$, obtained by passing acetylene into a solution of mercuric and sodium chlorides, yields aldehyde when treated with boiling dilute hydrochloric acid, and probably has the constitution $Hg{<}^{CCl_2}_{C(HgCl)_2}$.
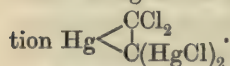
When sodium acetate, mercuric oxide, and potassium hydroxide are heated with water on a sand-bath until the oxide disappears, a yellowish-white substance is formed. When this is repeatedly digested with 5 per cent. aqueous potash, a *compound*, $(C_2Hg_2O_3H_2)_x$, is left undissolved, whilst the *hydroxydimercuracetic acid*, $OH\cdot CHg_2\cdot COOH$, goes into solution and forms a yellow, gelatinous precipitate when dilute nitric acid is added. The residue yields the compound $C_2Hg_2NO_5H$ when treated with 3 per cent. nitric acid. Dilute hydrochloric acid converts hydroxydimercuracetic acid into the *chloride*, $C_2Hg_2Cl_2O_2H_2$, and dilute nitric acid gives rise to the *nitrate*, $C_2Hg_2NO_5H$, which forms a yellowish-white powder.

The *compound* $C_2Hg_3IO_3H$, obtained by heating sodium acetate with mercuric iodide and caustic alkali, forms lustrous, greenish-white leaflets; the *sodium* salt is the direct product, and crystallises in yellow leaflets. The *compound* $C_2Hg_3NO_7H_3$ is prepared by the action of a dilute solution of silver nitrate.

The *compound* $HgCl\cdot CHCl\cdot COOK,KCl$, produced on heating aqueous potassium monochloracetate with mercuric oxide, crystallises from alcohol in slender, white needles.   M. O. F.

Mercury Derivatives of Nitrogen Compounds. By KARL A. HOFMANN and EDUARD C. MARBURG (*Annalen*, 1899, 305, 191—222).— The authors give evidence in favour of the formula $NH_2\cdot HgCl$ for the infusible white precipitate obtained when a solution of mercuric chloride is treated with ammonia. A boiling 20 per cent. solution of potassium hydroxide eliminates all the nitrogen from this substance in the form of ammonia; Kane's statement to the effect that only one-half is eliminated led Rammelsberg to suggest the formula NHg_2Cl,NH_4Cl.

The fusible white precipitate obtained when ammonia is added to a solution of mercuric chloride containing a large proportion of ammonium chloride has the constitution expressed by the formula $Hg(NH_3)_2Cl_2$; the formula $NHg_2Cl,3NH_4Cl$ has been put forward by Rammelsberg and Pesci, but the authors have found no reason for believing one atom of nitrogen to be in a condition of combination different from

that of the other. When the gases from nitric acid and arsenious oxide are passed into a suspension of the fusible, white precipitate in absolute alcohol, the salt is resolved into mercuric chloride and ammonia, yielding the double *compound*, $HgCl_2,2NH_4NO_3$, which crystallises from methylic alcohol in long, lustrous needles; hot sulphuric acid liberates chlorine. The double *compound*, $HgCl_2,2C_6H_4N_2SO_3$, obtained when a suspension of the fusible white precipitate and diazobenzene-sulphonic acid is allowed to remain at $10-15°$ during several days, forms straw-yellow crystals which decompose and dissolve in water, the whole of the nitrogen being liberated when the liquid is boiled; potassium hydroxide develops a yellow coloration, and sodium carbonate a reddish tint, whilst ammonia precipitates mercury and liberates nitrogen. The double *compound*, $Hg(CN)_2,2C_6H_4N_2SO_3$, prepared from mercuric cyanide and diazobenzenesulphonic acid, forms lustrous, prismatic crystals, and loses nitrogen when treated with boiling acids or alkalis; water at $60°$ resolves it into mercuric cyanide and diazo-benzenesulphonic acid.

Ethylamine forms three compounds with mercuric chloride, of which those having the formulæ $NHEt \cdot HgCl$ and $NH_2Et,HgCl_2$ have been prepared by Köhler. The double *compound*, $Hg(NH_2Et)_2Cl_2$, obtained on adding liquid ethylamine to alcoholic mercuric chloride, crystallises from alcohol in white leaflets and melts and decomposes at $185°$. The double *compound*, $NHMe_2,HgCl_2$, prepared from alcoholic solutions of dimethylamine and mercuric chloride, crystallises from boiling alcohol in nacreous leaflets, and melts at $172°$; aqueous solutions yield an orange yellow powder, having the composition $Hg_3Cl_2O_2,NHMe_2,HCl$. The double *compound*, $2NMe_3,3HgCl_2$, derived from mercuric chloride and trimethylamine, separates from alcohol in white crystals.

Millon's base is prepared from yellow mercuric oxide and aqueous ammonia, and may be regarded as dihydroxymercuriammonium hydroxide, $NH_2(Hg \cdot OH)_2 \cdot OH$; there is no justification for representing it by the formula $NHg_2 \cdot OH,2H_2O$, put forward by Rammelsberg. When the freshly prepared base is protected from light and dried over caustic potash in an atmosphere of ammonia, it becomes darker and more sensitive to light, and then has the composition $NHg_2O_2H_3$; if it is dried in a vacuum over sulphuric acid, ammonia is eliminated and a dark brown powder of the composition NHg_3O_2H is produced. Absolute alcohol dehydrates Millon's base, mercuric oxide being the final product; alcoholic ammonia, therefore, cannot be used in preparing the substance. The compound, $NHg_2 \cdot OH$, obtained by heating Millon's base at $125°$ in an atmosphere of ammonia, is a dark brown powder which explodes sharply on detonation, or when heated at $130°$; when exposed to air, it absorbs moisture, acquiring a lighter colour and losing its explosive properties. This explosive substance is also obtained when dried, yellow mercuric oxide is heated at $120°$ in an atmosphere of ammonia; it has been prepared also by Weyl. The nitrate, bromide, and chloride of Millon's base are described in the paper.

When the explosive compound, $N_2H_2Hg_2Cl_2$, obtained from hydrazine sulphate and mercuric chloride (Hofmann and Marburg, Abstr., 1897, ii, 554), is treated with acetic anhydride, it yields the *compound*

$NHg\cdot NAc_2$. *Diacetylhydrazine*, $N_2H_2Ac_2$, obtained by the action of hydrogen sulphide on this substance, crystallises from alcohol in lustrous leaflets and melts at $132°$; the *benzylidene* derivative crystallises from ether and melts at $113°$. On treating the compound $N_2H_2Hg_2Cl_2$ with chlorine in presence of carbon tetrachloride, it yields the compound $HgCl_2,N_2H_4,HCl$ in lustrous leaflets melting at $157°$.

The double *compound*, $N_2H_4,Cu(NO_3)_2$, is bluish-green, and explodes when heated and on detonation. M. O. F.

Aliphatic Sulphonic Acids. III. By ELMER P. KOHLER (*Amer. Chem. J.*, 1899, **21**, 349—370. Compare Abstr., 1898, i, 168, and this vol., i, 19).—α-Bromethylenesulphonic acid, $CH_2:CBr\cdot SO_3H$, is fairly stable in dilute aqueous solution, but when the solution is evaporated in a vacuum or over phosphoric anhydride a point is reached beyond which it is impossible to concentrate the acid without decomposition ensuing, hydrogen bromide and sulphurous anhydride being evolved. The *potassium, sodium*, and *barium* salts have all been obtained in the anhydrous form. *Bromethylenesulphonic chloride*, $CH_2:CBr\cdot SO_2Cl$, obtained by the action of phosphorus pentachloride on the potassium salt suspended in chloroform, is an oily liquid which cannot be distilled and which does not solidify at $-20°$. Oxidising agents convert the acid into carbonic anhydride, sulphuric acid, hydrogen bromide, and water. Reducing agents, both neutral and acid, convert the brom-acid quantitatively into ethylenesulphonic acid, and when an alkaline solution of the potassium salt is boiled with a large excess of mercuric chloride, the bromine is slowly replaced by chlorine.

Bromethylenesulphonic acid combines with water more readily even than does ethylenesulphonic acid, slow combination taking place when aqueous solutions of the acid or of its salts are boiled, whilst at $120°$ combination is complete in less than three hours. In the presence of a small quantity of an alkali carbonate, or an inorganic acid, addition takes place very readily at, or even below, $100°$, the product formed in all cases being *α-bromo-β-hydroxyethanesulphonic acid*. So far the acid has not been obtained in a crystalline form; the *sodium* salt crystallises from water in characteristic conical aggregates and the *potassium* salt in small, lustrous prisms containing $\frac{1}{2}H_2O$, which it loses below $150°$; when the anhydrous potassium salt is heated at $225°$ until the weight is constant, then dissolved in water, and alcohol added, potassium dibromodi-isethionate is precipitated. *Potassium α-bromo-β-acetoxyethanesulphonate* crystallises in small, lustrous needles, is readily soluble in water, but only sparingly in boiling alcohol.

Phosphorus pentachloride converts potassium bromohydroxyethanesulphonate into an oil, probably the lactone, $O{<}^{CH_2}_{SO_2}{>}CHBr$, which slowly dissolves in cold water yielding bromohydroxyethanesulphonic acid. When the same potassium salt is suspended in chloroform and treated with phosphorus pentachloride, *βα-chlorobromethanesulphonic chloride*, $C_2H_3ClBr\cdot SO_2Cl$, is obtained in the form of an oil, and this, when decomposed with water and neutralised with sodium hydroxide, yields the *sodium* salt, $C_2H_3ClBr\cdot SO_3Na$, which, on reduction with

zinc dust and water, yields sodium ethylenesulphonate. The constitution of bromohydroxyethanesulphonic acid follows from the fact that when reduced with dilute acid and sodium amalgam, isethionic acid (hydroxyethanesulphonic acid) is obtained ; when oxidised with potassium permanganate, it yields carbonic anhydride, water, hydrogen bromide, and sulphuric acid, whilst with nitric acid, it yields oxalic acid; with silver oxide, glycollic acid ; with barium manganate, *bromosulphoacetic acid*, the *barium* salt, $C_2HBrO_5SBa,2H_2O$, of which crystallises in colourless needles.

Potassium αβ-dibromethanesulphonate, readily obtained when potassium bromethylenesulphonate is heated with fuming hydrobromic acid at 120° for 5 hours, crystallises in compact, lustrous prisms moderately soluble in cold water, but insoluble in alcohol ; when reduced with zinc dust, ethylenesulphonic acid is formed, hence the two bromine atoms cannot be attached to the same carbon atom.

The nature of the products formed by the action of sulphuric acid on barium bromethylenesulphonate depends largely on the conditions. When the temperature is kept below 80° and only a slight excess of sulphuric acid is employed, the product is barium bromethionate, which, when boiled with water, yields barium sulphate and αβ-bromohydroxyethanesulphonic acid ; if the temperature is raised to 125° for a few hours and an excess of acid employed, a sulphonic acid is obtained, the *barium* salt of which, $(C_2H_2O_{10}BrS_3)_2Ba_3,4H_2O$, is sparingly soluble, crystallising in glistening plates ; the acid is probably a bromine derivative of the compound obtained by Rathke (this Journal, 1872, 388) by the action of acid sulphites on chloral. When boiled with water, the barium salt is decomposed, yielding barium sulphite and *barium acetaldehydedisulphonate*, $C_2HO_7BrS_2Ba,2H_2O$; the latter is decomposed by alkalis into barium formate and barium bromomethanedisulphonate, $CHBrS_2O_6Ba$.   J. J. S.

Oxidation of Alicyclic Compounds. Oxidation of Acetyltrimethylene. By M. IDZKOWSKA and E. WAGNER (*Chem. Centr.*, 1898, ii, 474—475 ; from *J. Russ. Chem. Soc.*, 1898, 30, 259—269). —An almost quantitative yield of acetyltrimethylene may be obtained by Lipp's method (Abstr., 1889, 843) if an aqueous solution of potassium hydroxide is used. Acetyltrimethylene boils at 113° under 753·5 mm. pressure, and on oxidation in aqueous solution with potassium permanganate, loses carbonic anhydride, and forms trimethylenecarboxylic acid, which is isolated as an oil by acidifying the filtrate with phosphoric acid and distilling with steam. The residue contains a small quantity of an acid, which, with phenylhydrazine, forms yellowish crystals, and hence is a ketonic acid, probably of the composition $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}{>}CH{\cdot}CO{\cdot}COOH$. The absence of formic, acetic, oxalic, malonic, and succinic acids proves that only acetyltrimethylene is formed from acetylpropylic bromide. The oxidation must take place directly without the intermediate formation of acetylpropylic alcohol, for neither acetopropionic nor acetic acid is found in the product.

In contrasting the oxidation of compounds containing open and closed chains, the authors point out that the methyl group of acetyltrimethylene is first oxidised, whilst in the case of methyl isopropyl ketone the CH-group is attacked, yielding acetic acid and acetone ; the former instance shows that the carbon atom, combined with the smallest number of hydrogen atoms, resists oxidation best.

According to E. Wagner, the hydrocarbon obtained by Gustavson (Abstr., 1896, i, 669) from penterythritol cannot be vinyltrimethylene, since it yields neither acetyltrimethylene nor trimethylenecarboxylic acid. From its products of oxidation, it appears to be a mixture of methylenetetramethylene and cyclopentene. The formation of acetyltrimethylene is the first instance of transition from the fatty to the polymethylene series by simple elimination of hydrogen bromide. Wolf's i-angelicalactone is probably, $COMe\cdot CH{<}^{CO}_{CH_2}$.

E. W. W.

Action of Hexachlorethane on Benzene in Presence of Aluminium Chloride. By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, [iii], **19**, 554—556).—When finely powdered aluminium chloride is gradually added to a solution of hexachlorethane in benzene heated at 70—75° in a reflux apparatus, hydrogen chloride is evolved and the mixture darkens in colour, becoming finally quite black. After washing with water and potash, the liquid, on distillation, yields small quantities of chlorobenzene and anthracene, besides unaltered benzene and hexachlorethane. The behaviour of hexachlorethane in this reaction is precisely what would be expected from the compound $CHCl_2\cdot CHCl_2$, a fact which is in keeping with the behaviour of other compounds, such as carbon tetrachloride and trichloracetic chloride, in which carbon is united to four radicles of a negative character. N. L.

Action of Pentachlorethane and of Tetrachlorethylene on Benzene in Presence of Aluminium Chloride. By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, [iii], **19**, 557—559).—When finely powdered aluminium chloride is gradually added to a solution of pentachlorethane in benzene heated at 70°, the liquid blackens, hydrogen chloride is evolved, and on distillation of the washed product, triphenylmethane and anthracene are obtained. Anthracene alone is produced when tetrachlorethylene is substituted for pentachlorethane. N. L.

Explanation of the Fittig Synthesis. III. Parabromotoluene and Sodium. By MAX WEILER (*Ber.*, 1899, **32**, 1056—1064. Compare Abstr., 1896, i, 237, 242).—Pure parabromotoluene was treated with sodium in toluene solution : 1600 grams yielded 145 grams of crude hydrocarbons boiling at 270—310°, from which about 50 grams of 4 : 4'-ditolyl were separated by repeatedly cooling and filtering, whilst 70 grams of an oil that would not crystallise remained ; this boiled at 283—288°. Besides these, large quantities of toluene and hydrocarbons containing more than two tolyl residues were formed.

The oil was oxidised repeatedly with chromic acid, the acids formed

and the ketones being removed each time, whilst the remaining neutral liquid was again submitted to oxidation. The ketones consisted of phenyl paratolyl ketone and another, or others, not isolated. The acids were separated by means of the difference (*a*) in volatility with steam of themselves or their methylic salts, and (*b*) in solubility of their barium salts; oxidation with alkaline permanganate being also employed. Those isolated were benzoic, terephthalic, isophthalic, and 4 : 4′-, 4 : 3′-, and perhaps traces of 3 : 3′-diphenyldicarboxylic acids. The original mixture of hydrocarbons must therefore have contained 4 : 4′- and 4 : 3′- (and 3 : 3′-?) ditolyl and 4-tolylphenylmethane; also dibenzyl, for some of this was left when a portion of the mixture was oxidised with chromyl chloride in carbon bisulphide solution (compare this vol., i, 519), and it is known that dibenzyl is attacked less readily than its isomerides under these circumstances. In the synthesis, the hydrocarbons were formed in about the following proportions:—Ditolyl : 4 : 4′- about 43 per cent.; 4 : 3′-, 6·5 per cent. or more; dibenzyl, about 2·5 per cent.; 4-tolylphenylmethane, 1 per cent. or more. The 4-bromotoluene had thus reacted as if it contained 3′-bromotoluene and benzylic bromide, although a pure substance was actually employed.

Diphenyl-4 : 3′-*dicarboxylic acid* was present amongst the acids not volatile with steam; these were converted into methylic salts, which were then treated with phenylhydrazine (to render non-volatile the methylic salts of any ketonic acids) and distilled with steam; the volatile portion was cooled, filtered from the methylic terephthalate that separated, and converted into barium salts, which were then crystallised fractionally; the acids from the less soluble fraction were oxidised with alkaline permanganate, and crystallisation of the barium salts was again employed; the more soluble salt was that of the acid in question, the less soluble being that of the 4 : 4′-isomeride. Diphenyl-4:3′-dicarboxylic acid melts at 333·5—334·5°, and its *dimethylic* salt at 98·5—99·5°; when oxidised with chromic acid in boiling acetic acid solution, it yields mainly terephthalic and some isophthalic acid.

Dimethylic ditolyl-4 : 4′-*dicarboxylate* was prepared incidentally, and for the first time, by treatment of the acid with phosphorus pentachloride and methylic alcohol; it melts at 212—213°.

<div align="right">C. F. B.</div>

Homologous Hydrocarbons of the Mesitylene Type. By LUDWIG GATTERMANN, SIGM. FRITZ, and K. BECK (*Ber.*, 1899, **32**, 1122—1127).—1 : 3 : 5-Triethylbenzene is best prepared by passing dry ethylene during 3—4 hours into a mixture of benzene and aluminium chloride heated on the water-bath in a reflux apparatus, and subsequently pouring on to powdered ice and fractionally distilling the product; the portion boiling between 200—215° consists of the nearly pure hydrocarbon. *Symmetrical triethylbenzamide*, $C_6H_2Et_3 \cdot CO \cdot NH_2$, prepared by the cyanuric acid method (this vol., i, 509), or, better, by gradually adding, at 0°, finely powdered aluminium chloride to a solution of 1 : 3 : 5-triethylbenzene and chloroformamide in carbon bisulphide, crystallises from light petroleum in colourless needles, melts at 155—156°, and is not changed by heating during several days with alcoholic potash; it is easily hydrolysed, however, by treatment with

nitrous acid (*loc. cit.*), giving rise to 2 : 4 : 6-*triethylbenzoic acid*, which crystallises from light petroleum in colourless, highly-refracting, monoclinic plates, melts at 113°, and yields no trace of the ethylic salt when heated for 4 hours on the water-bath with 3 per cent. alcoholic hydrogen chloride. The influence of a contiguous ethyl group in preventing etherification is thus the same as that of methyl in the cases studied by Victor Meyer and Sudborough. Pure 1 : 3 : 5-triethylbenzene, prepared from its carboxylic acid, boils at 218° and yields a *dinitro*-derivative, $C_{13}H_{16}N_2O_6$, which crystallises from light petroleum in short, yellow needles, and melts at 128—129°; *symmetrical tribromotriethylbenzene*, $C_{12}H_{15}Br_3$, separates from absolute alcohol in stout, colourless crystals and melts at 105—106°, whilst *symmetrical trinitrotriethylbenzene*, $C_{12}H_{15}N_3O_6$, forms silky, yellow needles, and melts and decomposes at 108—109°. *Diacetyltriethylbenzene*, $C_{16}H_{22}O_2$, prepared by warming at 30—40° a mixture of the hydrocarbon with acetic chloride, carbon bisulphide, and finely powdered aluminium chloride, separates from light petroleum in highly refracting, colourless crystals, and melts at 77°.

Symmetrical methyldiethylbenzene is conveniently prepared by passing ethylene into toluene in presence of aluminium chloride; the *methyldiethylbenzamide*, $C_{12}H_{17}NO$, obtained from it, crystallises from light petroleum in slender, colourless needles, melts at 106—107°, and, on hydrolysis with nitrous acid, yields the *acid*, $C_{12}H_{16}O_2$, which forms stout crystals, melts at 90—91°, and yields only traces of the ethereal salt when subjected to E. Fischer's etherification process; *trinitromethyldiethylbenzene*, $C_{12}H_{15}N_3O_6$, crystallises in yellow leaflets and melts at 86—87°.

1 : 3 : 5-*Dimethylethylbenzene*, prepared by passing ethylene into metaxylene containing aluminium chloride, boils at 185—195°, and yields a *dimethylethylbenzoic acid*, $C_6H_2Me_2Et\cdot COOH$, which crystallises from light petroleum in measurable crystals, melts at 101°, and does not form an ethereal salt when treated by Fischer's method; the *amide*, $C_6H_2Me_2Et\cdot CO\cdot NH_2$, forms colourless needles, and melts at 87·5°, whilst the *dinitro*-derivative, $C_{11}H_{12}N_2O_6$, crystallises from alcohol in yellow plates and melts at 154°.   W. A. D.

Phenylic Alkylic Phosphates. By ALBERT MOREL (*Compt rend.*, 1899, **128**, 507—510. Compare this vol., i, 29, 264).—When triphenylic phosphate is treated in presence of alcohol and ether with one mol. of sodium ethoxide, it yields diphenylic ethylic phosphate; with two molecular proportions, phenylic diethylic phosphate, and with three, diethylic sodium phosphate, phenylic ethylic ether, and sodium phenoxide.

The action of sodium ethoxide (1 mol.) on diphenylic ethylic phosphate (1 mol.) yields phenylic diethylic phosphate; that of sodium propoxide (1 mol.) yields phenylic ethylic propylic phosphate. The action of sodium ethoxide (2 mols.), however, does not yield triethylic phosphate, but diethylic phosphate and phenylic ethylic ether.

Triphenylic phosphate is not affected when boiled for a long time with alcohol or with alcoholic solutions of carbamide, quinoline, or pyridine.

A boiling solution of dimethylpiperazine in dilute alcohol converts triphenylic phosphate into diphenylic ethylic phosphate, but after prolonged boiling, or with a large excess of the base, the product is dimethylpiperazine phosphate.

The reaction with sodium ethoxide affords further illustration of the difference between the function of one hydroxyl of phosphoric acid and that of the other two, whilst dimethylpiperazine distinguishes between the two hydroxyls which behave similarly with sodium ethoxide. C. H. B.

Nitroquinone. By FRIEDRICH KEHRMANN and M. IDZKOWSKA (*Ber.*, 1899, **32**, 1065—1072).—In the preparation of orthonitroparamidophenol by the action of sulphuric acid on metanitrodiazobenzeneimide (Friedländer and Zeitlin, Abstr., 1894, i, 185), some of the 4 : 2-isomeride is formed, and remains in the mother liquor of the first substance. The oxidation of that substance does not yield 2-nitro-1 : 4-quinone (Abstr., 1895, i, 186); the product is in reality a substituted anilide of this, $NO_2 \cdot C_6H_2O_2 \cdot NH \cdot C_6H_3(NO_2) \cdot OH$ [$NH : NO_2 : O_2 = 1 : 3 : 2 : 5$ or $1 : 2 : 3 : 6$; $NH : NO_2 : OH = 1' : 3' : 4'$]. When heated with aniline, it undergoes a gradual transformation through the compound $NO_2 \cdot C_6HO_2(NHPh) \cdot NH \cdot C_6H_3(NO_2) \cdot OH$ [$NHPh = 4$] into the dianilidonitroquinone, $NO_2 \cdot C_6HO_2(NHPh)_2$, phenol being set free; the dianilido-compound is obtained pure only after prolonged treatment with aniline. When it is heated in acetic acid solution with fuming hydrochloric acid at the ordinary temperature, and the product oxidised with chromic acid, a dark brown *chloroquinone*, $C_{12}H_6ClN_3O_7$, is obtained. The dianilidonitroquinone is certainly a paradianilido-compound, for it is formed in small amount, together with much blue *nitranilidohydroxyquinoneanilide*, $NHPh \cdot C_6HO(NO_2)(OH) \vdots NPh$ [$1 : 2 : 6 : 4 : 5$], when the aniline salt of nitroparahydroxyquinone (Nietzki and Schmidt, Abstr., 1889, 968) is boiled with excess of aniline. C. F. B.

Ethanecatechol [Catechol Ethylenic Ether] and its Derivatives. By CHARLES MOUREU (*Bull. Soc. Chim.*, 1898, **19**, [iii], 507—511. Compare Abstr., 1898, i, 660, and this vol., i, 125).—The

alcohol, $C_6H_4 \begin{cases} O \cdot CH_2 \\ O \cdot CH \cdot CH_2 \cdot OH \end{cases}$, obtained by treating catechol with dibromohydrin in the presence of alkalis, crystallises in white needles, melts at 89—90°, and boils at 283—286°. The corresponding *acetate* boils at 185—188° under 30 mm. pressure.

Ethane protocatechuic aldehyde (*homopiperonal*), produced by the action of ethylenic dibromide on the disodium derivative of protocatechuic aldehyde, crystallises in silky needles, melts at 50—51·5°, and boils at 299°. The name homopiperonal is given to this substance on account of its relationship to piperonal, and from its mode of formation it must be represented by the formula $\begin{array}{c} CH\vdots CH \cdot C \cdot O \cdot CH_2 \\ COH \cdot C = CH \cdot C \cdot O \cdot CH_2 \end{array}$; the constitution of the related compounds being deduced from it. The *phenylhydrazone* of homopiperonal melts at 107—108°. The *aldoxime*

melts at 75—75·5°, and can be converted into *homopiperonylonitrile*, which crystallises in white needles and melts at 105°.

The nitro-derivative of catechol ethylenic ether, obtained by Vorländer (Abstr., 1895, i, 19), yields *amidocatechol ethylenic ether*, a heavy oil boiling at 162° under 9 mm. pressure; the *hydrochloride* decomposes at 220°, the *picrate* at 180°, and the *platinochloride* at 213°. When this amine is diazotised and treated with cuprous cyanide, it yields homopiperonylonitrile, hence the base has the following constitution:

$$\begin{array}{c} \text{CH:CH·C·O·CH}_2 \\ \text{NH}_2\text{·CH:CH·C·O·CH}_2 \end{array}$$
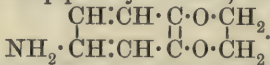
Homopiperonylic acid, obtained by hydrolysing the nitrile with alcoholic potash, melts at 137°. G. T. M.

Ethylenecatechol [Catechol Acetylenic Ether]. By CHARLES MOUREU (*Compt. rend.*, 1899, 128, 559—561).—Catechol acetylenic ether, $C_6H_4 \begin{smallmatrix} \text{O·CH} \\ \text{O·CH} \end{smallmatrix}$, obtained in small quantity by the action of acetic chloride on orthohydroxyphenoxyacetal, or on ethoxyethanecatechol, is readily prepared by dehydrating orthohydroxyphenoxyaldehyde with phosphoric anhydride in presence of quinoline. It is a colourless, neutral, oily liquid which boils at 76° under 13 mm. pressure and at 193° (corr.) under normal pressure, and has a sp. gr. 1·204 at 0°. When strongly cooled, it forms brilliant, white leaflets which melt between 16° and 20°. In presence of carbon bisulphide, it combines readily with bromine, without production of hydrogen bromide, and yields the dibromide, $C_6H_4 \begin{smallmatrix} \text{O·CHBr} \\ \text{O·CHBr} \end{smallmatrix}$, which crystallises from light petroleum in small, colourless prisms melting at 103—104·5°. In contact with hot water, this dibromide is converted into catechol, glyoxal, and hydrogen bromide. This reaction establishes the constitution of catechol acetylenic ether, which affords the first example of an unsaturated hexagonal nucleus containing two atoms of oxygen. C. H. B.

Methylethylenecatechol [Catechol Methylacetylenic Ether]. By CHARLES MOUREU (*Compt. rend.*, 1899, 128, 670—673. Compare Abstr., 1898, i, 644, 660; and this vol., i, 125, 138, 433, and preceding abstract). —*Catechol methylacetylenic ether*, $C_6H_4 \begin{smallmatrix} \text{O·CH} \\ \text{O·CMe} \end{smallmatrix}$, produced either by dehydrating 1-hydroxy-2-phenoxyacetone, $HO·C_6H_4·O·CH_2·COMe$, with phosphoric anhydride or by treating it with acetic chloride in the presence of ethylic orthoformate, is an oil distilling between 97° and 102° under 18 mm. pressure, or between 213° and 218° under ordinary pressures, and has a sp. gr. 1·1593 at 0°. It forms an unstable dibromide when treated with a cold solution of bromine in chloroform; the additive product, when boiled with water, decomposes, yielding catechol and hydrogen bromide; methylglyoxal, which should also result from this hydrolysis, could not be detected. G. T. M.

Synthesis of Estragole and of Allylic Compounds. By CHARLES MOUREU (*Bull. Soc. Chim.*, 1898, [iii], 19, 399—403).—A number of unsuccessful attempts were made to prepare estragole (paramethoxy-

allylbenzene) by heating a mixture of allylic iodide and anisoil with zinc powder, and by the action of allylic chloride, bromide, or iodide on par-iodanisoil or parabromanisoil in the presence of sodium and anhydrous ether. A vigorous and complex reaction occurs in each case, but estragole appears not to be formed. Estragole is probably produced when allylic chloride is gradually added to a solution of aluminium chloride in excess of anisoil, but in too small a quantity to admit of separation and identification. The chief product of the reaction is *dianisylpropane*, $C_3H_6(C_6H_4 \cdot OMe)_2$, a white, odourless, crystalline solid which melts at $68-69°$, boils at about $200°$ under 10 mm. pressure, and yields paramethoxybenzoic acid on oxidation with dilute nitric acid. This compound is evidently formed by the action of the estragole first produced on the excess of anisoil present, possibly with the intermediate formation of chloropropylanisoil. It seems probable that the synthesis of estragole might be effected by the action of sodium allyloxide on sodium paramethoxybenzenesulphonate or on the corresponding sulphinate. Anisoil and phenetoil are readily obtained by distilling a mixture in molecular proportion of sodium benzenesulphonate with sodium methoxide and ethoxide respectively, but experiments with sodium benzenesulphinate seem to show that the use of this substance is impracticable. N. L.

Oxidation of Organic Bases with Hydrogen Peroxide. By RICHARD WOLFFENSTEIN (*Ber.*, 1899, **32**, 688—689).—Surprise is expressed that Bamberger and Tschirner (this vol., i, 348) should have investigated the action of hydrogen peroxide on tertiary bases, as this forms a natural continuation of the work of Wernick and the author (Abstr., 1898, i, 536). C. F. B.

Oxidation of Aromatic Bases. By EUGEN BAMBERGER (*Ber.*, 1899, **32**, 1159—1161).—A reply to Wolffenstein (preceding abstract). W. A. D.

Derivatives of Paramidophenol. By OSCAR HINSBERG (*Annalen*, 1899, **305**, 276—289).—N-*Methylphenacetin*, $OEt \cdot C_6H_4 \cdot NMeAc$, prepared by adding slight excess of methylic iodide to xylene in which the sodium derivative of phenacetin is suspended, separates from light petroleum in colourless crystals and melts at $41°$; contact with water transforms it into an oil which dissolves in a large proportion of water. It is noteworthy that the narcotic action of phenacetin is considerably increased by introducing the methyl group.

N-*Ethylphenacetin*, $OEt \cdot C_6H_4 \cdot NEtAc$, melts at $38°$, and resembles the methylic derivative in taste and odour; it is a more powerful narcotic than the foregoing substance.

N-*Isopropylphenacetin*, $OEt \cdot C_6H_4 \cdot NPr\beta Ac$, is a colourless, viscous oil, readily soluble in alcohol, ether, and benzene, and dissolving also in 260 parts of water at $30°$. The narcotic action of isopropyl-phenacetin and the higher homologues is less powerful than that of the methylic and ethylic derivatives.

Acetamidophenylic propylic ether, $OPr^a \cdot C_6H_4 \cdot NHAc$, prepared from acetamidophenol, alcoholic soda, and propylic iodide, crystallises from

dilute alcohol in colourless leaflets, and melts at 122°; as a febrifuge, its action is feebler than that of phenacetin.

ω-*Bromophenacetin*, $CH_2Br \cdot CH_2 \cdot O \cdot C_6H_4 \cdot NHAc$, obtained by heating acetamidophenol with ethylenic bromide and caustic soda, crystallises from dilute alcohol in white needles and melts at 130°. When heated with sodium salicylate at 160—180°, it yields the *salicylic* derivative of ω-hydroxyphenacetin,

$$OH \cdot C_6H_4 \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot C_6H_4 \cdot NHAc,$$
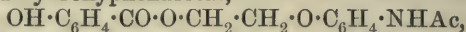
which crystallises from alcohol, and melts at 133°.

Acetamidophenylic ethylic carbonate, $COOEt \cdot O \cdot C_6H_4 \cdot NHAc$, prepared from acetamidophenol, caustic soda, and ethylic chlorocarbonate, crystallises from dilute alcohol in colourless needles and melts at 121°.

N-*Ethylacetamidophenol*, $OH \cdot C_6H_4 \cdot NEtAc$, crystallises from alcohol in colourless needles and melts at 187°; the *acetyl* derivative crystallises from light petroleum or ether, and melts at 58°. The ethylamidophenol from which ethylacetamidophenol is prepared can be obtained by the action of concentrated hydrochloric acid on ethylphenacetin at 220—240°, and also by gently heating paramidophenol in alcoholic solution with ethylic bromide (1 mol.).

Parahydroxyphenylurethane ethylic carbonate,

$$COOEt \cdot O \cdot C_6H_4 \cdot NH \cdot COOEt,$$
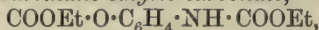
produced by the action of ethylic chlorocarbonate on paramidophenol in dilute caustic soda, crystallises from dilute alcohol in colourless needles and melts at 108—109°.

Parahydroxyphenylethylurethane ethylic carbonate,

$$COOEt \cdot O \cdot C_6H_4 \cdot NEt \cdot COOEt,$$
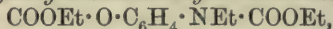
prepared from ethylparamidophenol and ethylic chlorocarbonate, separates from dilute alcohol in colourless crystals and melts at 60—62°.

Paramidophenylic hydrogen tartrate separates from water in large, transparent crystals, and decomposes at 216°.   M. O. F.

1 : 3 : 2-Metaxylidine. By MAX BUSCH (*Ber.*, 1899, **32**, 1008—1012). —*Formylmetaxylidide* [$Me_2 : NH \cdot CHO = 1 : 3 : 2$] crystallises from alcohol in white, silky needles and melts at 159—160°. 1 : 3 : 2-*Benzylidenemetaxylidine* is a yellow oil; its formation takes place more slowly than in those cases where the ortho-positions are occupied by hydrogen. *Metanitrobenzylidene*-1 : 3 : 2-*metaxylidine* separates from alcohol in yellow crystals and melts at 105°; the *orthonitro*-compound forms reddish-brown crystals. *Orthohydroxybenzylidene*-1 : 3 : 2-*metaxylidine* is a yellow oil. *Dixylylthiocarbamide*, $CS(NH \cdot C_8H_9)_2$, crystallises from alcohol in transparent prisms and melts at 231°. *Xylylthiocarbimide* is a thick, transparent oil which solidifies to flaky crystals and melts at the temperature of the hand; it behaves in the normal way towards amines and hydrazines. *Phenylxylylthiocarbamide* crystallises from alcohol in slender, white needles, dissolves most readily in boiling acetic acid, and melts at 204°. 1-*Phenyl-4-xylylthiosemicarbazide*, $NHPh \cdot NH \cdot CS \cdot NH \cdot C_8H_9$, separates from alcohol in colourless crystals, and melts and decomposes at 210°.

1 : 3 : 2-*Xylylhydrazine* crystallises from light petroleum in glisten-

ing, white needles, and melts at 46°; it decomposes gradually, forming a brown oil. *Benzylidenexylylhydrazine* is an unstable, yellow oil. *Metanitrobenzylidenexylylhydrazine* separates from alcohol in orange-coloured needles and melts at 119—120°. 4-*Phenyl-1-xylylthiosemicarbazide*, $C_8H_9 \cdot NH \cdot NH \cdot CS \cdot NHPh$, forms glistening, white needles, melts at 181—182°, and is insoluble in ether and benzene, but dissolves slightly in alcohol, and more readily in boiling acetic acid. T. M. L.

Derivatives of β-Bromopropylamine. By AUGUST UEDINCK (*Ber.*, 1899, **32**, 967—979).—β-Bromopropylbenzamide is obtained when β-bromopropylamine hydrobromide is treated with benzoic chloride by the Schotten-Baumann method. μ-Phenyl-β-methyl-oxazoline (Abstr., 1891, 1267) may be obtained by mixing the amide with boiling water and potassium hydroxide, and immediately distilling in a current of steam; the yield is 60—66 per cent. of the theoretical. From the residue, β-hydroxypropylbenzamide (Abstr., 1891, 860) may be obtained by evaporation.

Benzyl-β-hydroxypropylamine, $OH \cdot CHMe \cdot CH_2 \cdot NH \cdot CH_2Ph$, is formed when the oxazoline is reduced with sodium and ethylic alcohol, the alcohol and unaltered oxazoline removed by distillation in steam, and the base purified by solution in oxalic acid and subsequent distillation under diminished pressure; it is a thick, colourless, strongly refractive liquid which boils at 136—140°, 143—146°, 147—149°, and 151—154° under pressures of 7, 13, 15, and 19 mm. respectively, has a sp. gr. 1·84 at 17·5°/4°, is moderately soluble in water, yielding a strongly alkaline solution, and absorbs both moisture and carbonic anhydride from the atmosphere. Its *hydrochloride* crystallises in thin, rectangular plates melting at 119—120°, and readily soluble in alcohol, chloroform, or water; its *hydrobromide* in glistening plates melting at 122°, and its *hydriodide* at 119°. The *picrate*, $C_{10}H_{15}NO, C_6H_3N_3O_7$, forms small plates melting at 127—128°; the *platinochloride* crystallises in dark red, rhombic plates melting and decomposing at 185°; the *aurichloride* forms small, yellow plates melting at 114°, and the *nitrosamine*, $C_{10}H_{14}ON \cdot NO$, is a dark yellow oil.

Benzyl-β-chloropropylamine hydrochloride,
$$CHMeCl \cdot CH_2 \cdot NH \cdot CH_2Ph, HCl,$$
is obtained when benzyl-β-hydroxypropylamine hydrochloride is heated with an excess of the strongest hydrochloric acid for 8 days at 100°; after purification by solution in absolute alcohol and precipitation with ether, it forms small, glistening scales melting at 158—159°. The *picrate* crystallises in small, yellow, lozenge-shaped plates. *Benzyl-β-iodopropylamine hydriodide* crystallises from hot water in colourless, rectangular plates melting at 168—169°, and yields a *picrate* melting at 111—112°. *Benzyl-β-bromopropylamine hydrobromide* crystallises in colourless scales, melts at 170—171°, and yields a *picrate* crystallising in yellow needles and melting at 125—126°.
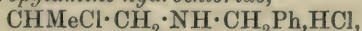
Dibenzyldimethylpiperazine, $CH_2Ph \cdot N \!\!<\!\! {}^{CH_2 \cdot CHMe}_{CHMe \cdot CH_2} \!\!>\!\! N \cdot CH_2Ph$,
may be isolated from the brown residue obtained when the last hydrobromide is treated with potassium hydroxide and immediately distilled

in steam; it crystallises from ether in thin, transparent, rhombic plates melting at 105—106°, and yields sparingly soluble salts. The yield of base is poor, as the alkali converts part of the β-bromo-compound into benzyl-β-hydroxypropylamine.

The compound formerly described as *n*-benzylethylene-ψ-thiocarbamide (Abstr., 1896, ·i, 702) should be *v*-benzylethylene-ψ-thiocarbamide, $\begin{smallmatrix} CH_2 & ---S \\ | & \\ CH_2 \cdot N(C_7H_7) \end{smallmatrix}\!\!>\!C\!:\!NH$; the corresponding *propylene* derivative, $\begin{smallmatrix} CHMe & ---S \\ | & \\ CH_2 \cdot N(C_7H_7) \end{smallmatrix}\!\!>\!C\!:\!NH$, is obtained in the form of its *thiocyanate* by the action of potassium thiocyanate on β-bromopropylbenzylamine hydrobromide; the salt crystallises in tufts of needles melting at 126—127°. The *base* is a thick, yellow oil of alkaline reaction and readily soluble in the usual organic solvents. The *hydrochloride* crystallises in glistening, rhombic plates melting at 215—216°, the *aurichloride* in lemon-yellow needles melting and decomposing at 146—148°, the *platinochloride* in short, orange-red prisms melting and decomposing at 216—218°, and the *picrate* in dark yellow needles melting at 117—119°. When oxidised by Andreasch's method, (Abstr., 1883, 664), the base yields a compound, $C_{11}H_{13}N_2ClSO_2$, crystallising in colourless needles and melting at 125—126°, to which the authors assign the constitution $\begin{smallmatrix} CHMe & ---SO_2 \\ | & \\ CH_2 \cdot N(CH_2Et) \end{smallmatrix}\!\!>\!C\!:\!NCl$.

βμ-Dimethyloxazoline, $\begin{smallmatrix} CHMe \cdot O \\ | \\ CH_2 & --N \end{smallmatrix}\!\!>\!CMe$, obtained when β-bromopropylamine hydrobromide is boiled for 3 hours with three times its weight of acetic anhydride, forms a mobile liquid boiling at 117—119°. The *picrate* melts at 114—115°, the *platinochloride* forms orange-yellow needles, readily soluble in water, and melting and decomposing at 188—190°. When an aqueous solution of the hydrochloride of the base is heated, hydrolysis ensues and *β-amidoisopropylic acetate* OAc·CHMe·CH$_2$·NH$_2$, is obtained as a clear syrup, which yields a *platinochloride* melting and decomposing at 207—209°.

β-Bromopropylorthonitrobenzamide,
CHMeBr·CH$_2$·NH·CO·C$_6$H$_4$·NO$_2$,
obtained by the action of orthonitrobenzoic chloride on β-bromopropylamine hydrobromide, crystallises from benzene in long needles melting at 104—105°, and when treated according to Elfeldt's method (Abstr., 1892, 213), yields *μ-orthonitrophenyl-β-methyloxazoline*, $\begin{smallmatrix} CHMe \cdot O \\ | \\ CH_2 & --N \end{smallmatrix}\!\!>\!C \cdot C_6H_4 \cdot NO_2$, as a colourless liquid with a pleasant odour, distilling at 173—176° under 8 mm. pressure. The *hydrochloride*, $C_{10}H_{10}N_2O_3,HCl$, crystallises in long, slender needles melting at 119—120°; the *picrate* in yellow needles melting at 129—130°, and the *platinochloride* in dark orange-yellow needles melting and decomposing at 187—188°.
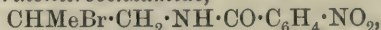
Amidoisopropylic orthonitrobenzoate yields a *platinochloride* which crystallises in short, pale orange-yellow needles melting and decomposing at 215°, and a *picrate* melting at 176—178°. *β-Bromopropylparanitro-*

benzamide crystallises from benzene or absolute alcohol in greenish-yellow needles melting at 135°. *μ-Paranitrophenyl-β-methyloxazoline* crystallises from 70 per cent. alcohol in thin, rectangular plates melting at 134—135°; it yields a *platinochloride*, crystallising in dark reddish-yellow needles melting and decomposing at 192°, and a *picrate* melting at 185—186°. *Amidoisopropylic paranitrobenzoate* crystallises from hot water in glistening scales, melting at 167—168°; its *hydro-chloride* melts at 191—192°, its *platinochloride* melts and decomposes at 191—193°, and its *picrate* melts at 168—169°.   J. J. S.

Paradihydroxydiphenylamine. By FELIX SCHNEIDER (*Ber.*, 1899, **32**, 689—691).—*Paradihydroxydiphenylamine*, $NH(C_6H_4 \cdot OH)_2$, is obtained by heating quinol with ammonium chloride and caustic soda for seven hours, first at 160°, then at 180°; or by heating quinol with paramidophenol and fused calcium chloride for 5 hours at 160—180°. In the first case, the product is boiled with 1 per cent. hydrochloric acid, the solution is filtered, unchanged quinol is removed by extraction with ether, and then the base is precipitated by the addition of sodium acetate. In the second case, the product is dissolved in water, the solution decolorised by the addition of a few drops of hydrochloric acid, boiled, filtered, and set aside to crystallise. In both cases, the crude product is recrystallised from water. It melts at 174·5°, gives a blue solution in concentrated sulphuric acid, changing to brown when diluted, dissolves in acids and in alkalis with a blue colour, doubtless owing to oxidation to indophenol, $O:C_6H_4:N \cdot C_6H_4 \cdot OH$, of which it is the leuco-compound; it is also oxidised to this substance in benzene solution by mercuric oxide. It forms a *triacetyl* derivative melting at 128·5°.

From quinol and paraphenylenediamine, in the presence of dehydrating agents, a *compound*, apparently $NH_2 \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot OH, 2HCl$, was eventually obtained; it melted and decomposed above 190°:
        C. F. B.

Formation of Dimethylaniline by the Action of Bromo- or Iodo-benzene and Phenol on Dimethylamine. By BORIS N. MENSCHUTKIN (*Chem. Centr.*, 1898, ii, 478—479; from *J. Russ. Chem. Soc.*, 1898, **30**, 243—251).—When bromo- or iodo-benzene is heated with dimethylamine at 250—260° for 5—6 days, the product contains dimethylaniline; this is also obtained by heating phenol with dimethylamine at 250° for 60—84 hours. By adding potassium hydroxide to the product after all the free dimethylamine has been removed, a further quantity of dimethylamine is formed, probably owing to the decomposition of a phenolate of the amine $NHMe_2, PhOH$.

An almost theoretical yield of dimethylamine hydrochloride is obtained by adding powdered nitrosodimethylaniline hydrochloride and a few zinc shavings to a nearly boiling, dilute aqueous solution of sodium hydroxide; the amine is absorbed in a Péligot's U-tube containing concentrated hydrochloric acid.   E. W. W.

Salts of Methyl- and Dimethyl-aniline with Halogen Acids. By BORIS N. MENSCHUTKIN (*Chem. Centr.*, 1898, ii, 479; from *J. Russ. Chem. Soc.*, 1898, **30**, 251—259).—Dimethylaniline hydrochloride

prepared from dry hydrogen chloride and dimethylaniline, can be purified by freezing in benzene solution; it separates from benzene in white, crystalline flakes melting at 85°, but can be crystallised from aqueous solution in long, thin plates melting at 80—81°. The hydrobromide melts at 75°. The hydriodide, prepared from dry hydrogen iodide and commercial dimethylaniline and washed with benzene, in which it is insoluble, melts at 112° and forms crystals which are affected by light; it separates from water in white crystals, like octahedra, and then melts at 111°. Pure dimethylaniline is best prepared from this salt; it melts at 2·5°, boils at 192·5° under 761 mm. pressure, and has a sp. gr. 0·9580 at 18°.

Methylaniline hydrochloride, prepared like the corresponding dimethylaniline salt, separates in white crystals, melts at 121—122°, is not hygroscopic, and is insoluble in benzene. The hydrobromide melts at 98°. The hydriodide separates in crystals, melts at 124°, and is insoluble in benzene.

Hydrogen bromide can be prepared by adding bromine to a cold mixture of iron powder (ferrum alcoholisatum), copper sulphate, and benzene.   E. W. W.

Amido-amidines. IV. By FERNAND MUTTELET (*Bull. Soc. Chim.*, 1898, **19**, [iii], 519—520. Compare this vol., i, 354).—Benzodinitranilide, obtained by heating dinitraniline $[NH_2 : NO_2 : NO_2 = 1 : 2 : 4]$ with benzoic chloride at 170—180°, separates from hot toluene in yellow, granular crystals and melts at 220°. The *amido-amidine*,

$$NH_2 \cdot C_6H_3 \!\!<^{-N}_{NH}\!\!> CPh,$$
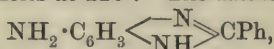
produced by reducing the preceding compound, crystallises from dilute alcohol in pink granules and melts at 286—288°; it is isomeric with an amidine obtained by Lauth (Abstr., 1897, i, 516).   G. T. M.

Substantive Azo-dyes of the Benzimidazole Series. By JOHANNES PINNOW and F. WISKOTT (*Ber.*, 1899, **32**, 898—915).—Nitroorthophenylenediamine reacts with benzaldehyde in alcoholic solution forming two compounds. *Benzenylnitrophenyleneamidine* (3-nitro-2'-phenylbenzimidazole, $NO_2 \cdot C_6H_3 \!\!<^{NH}_{N}\!\!> CPh$, is soluble in potash, and crystallises in almost colourless needles melting at 203°. *Nitrobenzaldehydine* (3-nitro-2'-phenyl-1'-benzylbenzimidazole),

$$N \!\!<^{C_6H_3(NO_2)}_{CPh\text{-}} \!\!> N \cdot CH_2Ph,$$
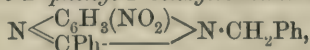
is insoluble in potash and crystallises in light yellow needles melting at 187—188°; two isomeric forms of this compound are probably produced. *Amidobenzaldehydine* is formed by the reduction of the nitro-compound and crystallises in colourless prisms melting at 192° (Hinsberg's compound melted at 121°; Abstr., 1896, i, 537). The *hydrobromide* crystallises with $5H_2O$, the *picrate* melts at 231°, and the *acetyl* derivative at 214°. The base is readily converted into a diazo-salt which reacts with phenol to form *benzaldehydine-azophenol*, $C_{26}H_{20}N_4O$, a yellow, crystalline powder melting at 273°. Benzenyl-amidophenyleneamidine (2'-phenylamidobenzimidazole) crystallises in plates, which do not melt below 280°, and has been obtained by

Muttelet (preceding abstract) by the reduction of benzo-a-dinitranilide. The *hydrobromide* crystallises in prisms, the *picrate* melts at 220°, and the *acetyl* derivative at 241°. The base readily yields colouring matters, such as *phenylbenzimidazoleazodimethylaniline*, a yellow, crystalline powder melting at 268°.

Orthophenylenediamine reacts with metanitrobenzaldehyde forming *nitrobenzenylphenyleneamidine* (*metanitro-2'-phenylbenzimidazole*) $C_{13}H_9N_3O_2$, which crystallises in needles or prisms melting at 204—205°. *2'-Nitrophenyl-1'-nitrobenzylbenzimidazole* is also formed in this reaction and crystallises in prisms or pyramids melting at 170—171°. *Amidobenzenylphenyleneamidine* crystallises in needles decomposing at 220°, and yields an *acetyl* derivative decomposing at 250°. The base readily yields colouring matters with metaphenylene-diamine and with a-naphthol. *Diamidobenzaldehydine* crystallises in prisms melting at 194°, and forms a *diacetyl* derivative melting at 219°. Both the amido-groups undergo the diazo-reaction readily. When treated with metanitrobenzaldehyde, nitro-orthophenylenediamine yields *trinitrobenzaldehydine* (1'-nitrobenzyl-2'-nitrophenyl-3-nitrobenz-*imidazole*), $N{<}^{C_6H_3(NO_2)-}_{C(C_6H_4 \cdot NO_2)}{>}N \cdot CH_2 \cdot C_6H_4 \cdot NO_2$, melting at 236°, along with *nitrobenzenylnitrophenyleneamidine* (*2'-nitrophenyl-3-nitro-benzimidazole*), $NO_2 \cdot C_6H_3{<}^{NH}_{-N}{>}C \cdot C_6H_4 \cdot NO_2$, which melts at 283° and is soluble in alkalis. *Triamidobenzaldehydine hydrochloride* crystallises in slender needles which decompose above 250°, and when treated with sodium acetate yield the *monacetate*, and not the free base; the *triacetyl* derivative crystallises in needles melting at 178—179°. All three amido-groups readily undergo the diazo-reaction, and the base, therefore, yields a colouring matter containing three naphthol groups. The reduction of nitrobenzenylnitrophenylene-amidine does not yield the corresponding base, but a compound, $C_{13}H_{12}N_4O + H_2O$, which is probably an oxydiamidophenylbenz-imidazole, the *acetyl* derivative being a crystalline powder and melting at 150°. An attempt was made to ascertain the exact constitution of nitrobenzaldehydine by synthesis from a-dinitrodibenzylaniline; oxidation with chromic acid, however, does not remove a benzyl group from this compound, as might be expected, but yields a-dinitraniline.

Comparative dyeing experiments were carried out with the various colouring matters obtained from the bases described, and it was found that: 1. The fastness of the colouring matter increases with the number of azo-groups present. 2. An azo-group in the benzimidazole ring is more efficacious in producing a fast colour than one in the benzyl or phenyl group. 3. Compounds containing the azo-group in the benzimidazole ring give brown or bluish-brown shades; those containing it in the other groups produce yellowish or reddish-brown shades. / A. H.

Combination of Phenylhydrazine and Alkylic Iodides. By P. Genvresse and Paul Bourcet (*Compt. rend.*, 1899, 128, 564—566). —The violent reaction between phenylhydrazine and alkylic iodides can be moderated by means of solvents such as alcohol or ether.

Methylic iodide yields two compounds: the first, $N_2H_2Me_2PhI$, forms long, monoclinic prisms, which melt and decompose at 122°, dissolve in water, especially if hot, but are almost insoluble in alcohol, and insoluble in ether. It is practically not attacked by hot concentrated potassium hydroxide solution, but reacts with silver oxide; gives a blue precipitate with Fehling's solution, but does not reduce it, a white precipitate with mercuric chloride, a pale yellow precipitate with lead acetate, a yellow precipitate with silver nitrate insoluble in sodium thiosulphate, a red precipitate with cupric sulphate, and a rust-coloured precipitate with ferric chloride. The second compound, $2N_2H_3Ph,MeI$, forms slender, white needles soluble in alcohol and very soluble in water, but insoluble in ether; it melts and decomposes at 125°. It reduces Fehling's solution, silver nitrate, and gold and platinum chlorides. Both compounds are somewhat unstable, but the second is much more liable to decompose than the first.

Ethylic iodide yields analogous compounds, which, however, are more readily purified and are much more stable; the compound insoluble in alcohol melts and decomposes at 116°, and the other melts to a yellow liquid at 27°.   C. H. B.

Oxidation of Benzaldehydephenylhydrazone and Salicylaldehydephenylhydrazone by Air. By HEINRICH BILTZ (*Annalen*, 1899, **305**, 165—187. Compare Abstr., 1894, i, 584).—The compound described as a polymeride of salicylaldehydephenylhydrazone (*loc. cit.*) is not formed under conditions which preclude the possibility of oxidation; it may be obtained from a more labile isomeride arising from salicylaldehydephenylhydrazone on oxidation, and probably consists of salicilosazone, $C_2(C_6H_4 \cdot OH)_2(N_2HPh)_2$, because benzaldehydephenylhydrazone yields α-benzilosazone when oxidised by air.

The transformation of benzaldehydephenylhydrazone into α-benzilosazone is effected by passing a current of air into a solution of the aldehyde derivative in alcoholic potash heated in a reflux apparatus; the osazone has the properties described by Ingle and Mann (Trans., 1895, **67**, 606). The *acetyl* derivative is very readily soluble in chloroform, carbon bisulphide, acetic anhydride, and ethylic acetate, but dissolves with difficulty in methylic and ethylic alcohols; it melts indefinitely at 80—90°, not having been obtained crystalline. The *acetyl* derivative of β-benzilosazone crystallises from alcohol in thin leaflets, and melts at 183—185°.

Salicil-α-osazone, $C_2(C_6H_4 \cdot OH)_2(N_2HPh)_2$, prepared by oxidising salicylaldehydephenylhydrazone in alcoholic potash by air at the ordinary temperature, crystallises from ethylic acetate in aggregates of microscopic plates and melts at 227—228°; concentrated sulphuric acid develops an orange-red coloration, which rapidly darkens and ultimately becomes greenish. The *triacetyl* derivative cannot be recrystallised, and yields salicil-β-osazone on hydrolysis. The *compound*, $C_{19}H_{13}N_2O_2$, is a bye-product in the formation of salicil-α-osazone; on adding alcohol to the solution in nitrobenzene, it crystallises in slender, deep red needles and melts at 184°. The solution in concentrated sulphuric acid is purple-violet.

Salicil-β-osazone has been already described as a polymeric salicyl-aldehydephenylhydrazone (*loc. cit.*), and is obtained on treating the α-derivative with hot nitrobenzene, from which it crystallises in mono-clinic leaflets melting at 281—282°. The *tetracetyl* derivative crystallises from ethylic acetate and melts at 244°.　　　　　M. O. F.

Nitrosalicylaldehydephenylhydrazones. By HEINRICH BILTZ (*Annalen*, 1899, **305**, 187—190).—5-*Nitrosalicylaldehydephenylhydrazone*, $NO_2 \cdot C_6H_3(OH) \cdot CH:N_2HPh$ [$CH:OH:NO_2 = 1:2:5$], crystallises from alcohol in rhombic, fluorescent leaflets, and melts at 194°; the *acetyl* derivative, which is not phenolic, melts at 165—166°, and yields a *silver* derivative. 3-*Nitrosalicylaldehydephenylhydrazone*, [$CH:OH:NO_2 = 1:2:3$], crystallises from alcohol in dark red, rhombic plates, and melts at 138°; the *acetyl* derivative forms yellowish, pleochroic needles, and melts at 150°.　　　　　M. O. F.

Stereoisomeric Thiosemicarbazides. II. By WILHELM MARCKWALD (*Ber.*, 1899, **32**, 1081—1087. Compare Abstr., 1893, i, 26).—As previously described, a thiosemicarbazide, $NHR^{(1)} \cdot N:C(SH) \cdot NHR^{(4)}$, is obtained by allowing a hydrazine, $NHR^{(1)} \cdot NH_2$, to remain with a thiocarbimide, $CS:NR^{(4)}$, in alcoholic solution at the ordinary temperature. Frequently it exists in two stereoisomeric forms, the unstable anti-form, which is first obtained, changing to the more stable syn-form when a little hydrochloric acid is added to its alcoholic solution, or when it is fused or subjected to prolonged heating.

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$$NHR^{(1)} \cdot N$$
$$NHR^{(4)} \cdot C \cdot SH$$
Unstable, anti-form (α).

$$N \cdot NHR^{(1)}$$
$$NHR^{(4)} \cdot C \cdot SH$$
Stable, syn-form (β).

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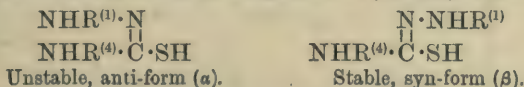
These two forms are distinguished by treating a few centigrams with a benzene solution of carbonyl chloride, allowing the liquid to evaporate, warming the residue with ammonia, filtering and acidifying the filtrate with hydrochloric acid; if a precipitate forms, the original substance was an anti-compound, but if nothing more than an opalescence, a syn-compound. With carbonyl chloride, the syn-compound yields a thiobiazolone, which is neither acid nor basic in character, whilst the anti-form yields an imidobiazolone of acid character (in addition to some thiobiazolone, which probably results from a partial transformation of the anti- into the syn-form).

<div style="display:flex;justify-content:space-around">

$$CO < \begin{matrix} NR^{(1)} \cdot N \\ NR^{(4)} \cdot C \cdot SH \end{matrix}$$
Imidobiazolone.

$$\begin{matrix} N \cdot NR^{(1)} \\ NHR^{(4)} \cdot C \cdot S \end{matrix} > CO$$
Thiobiazolone.

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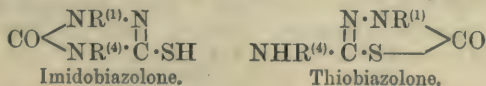
A great number of thiosemicarbazides has been prepared, and the following regularities have been observed with respect to the possibility of isomerism. (1.) Phenylhydrazine always unites with thiocarbimides, yielding unstable thiosemicarbazides of the anti-form, which are transformed into the stable syn-form when boiled with hydrogen chloride in alcoholic solution. (In this connection, it is noteworthy that 1-naphthylthiocarbimide forms no anti-thiosemicarbazides; 2-naphthylthiocarbimide, only very unstable ones, and none at all with phenylhydrazine itself). (2.) When the para-position in phenylhydrazine is

occupied, the resulting hydrazines behave like the parent substance. (3.) When the ortho- or meta-position is occupied, only stable thiosemicarbazides of the syn-form exist.   (As might be anticipated from this, 1- and 2-naphthylhydrazines yield only syn-thiosemicarbazides ; in the case of 1-naphthylhydrazine and phenylthiocarbimide, an isomeride melting at 135° is, indeed, obtained, but it, like the other compound, yields the thiobiazolone when treated with carbonyl chloride). (4.) The capacity for forming stereoisomeric thiosemicarbazides is entirely independent of the nature of the thiocarbimide, whether aliphatic or aromatic, and, in the latter case, whether substituted in the ortho-, meta-, or para-position. (5.) The unstable anti-compounds always melt at lower temperatures than the stable stereoisomerides.   (6.) Secondary hydrazines are incapable of yielding stereoisomeric forms.

The compounds obtained are enumerated, with their melting points, in the following table ; a few of them have been described already, but most are new.   The carbonyl chloride test was performed with all the thiosemicarbazides, but the melting point of the derivative obtained is only quoted when the latter was analysed.

$R^{(1)}$.	$R^{(4)}$.	Thiosemicarbazide.		Imido-biazolone.	Thio-biazolone.
		Anti.	Syn.		
Phenyl	Methyl	90—91°	163—164°	208°	240°
,,	Phenyl	139	176	219—221	188
,,	2-Tolyl	134	164	—	—
,,	4- ,,	150	176	—	—
,,	2 : 4-Xylyl	145	159	262	126
,,	3-Chlorophenyl	120	168	—	—
,,	4- ,,	133	165	—	—
4-Tolyl	Methyl	119	169—170	—	—
,,	Phenyl	123	175	—	—
,,	2-Tolyl	130—131	162—163	—	—
,,	4- ,,	124—125	154	—	—
,,	2 : 4-Xylyl	152	170	—	—
,,	4-Chlorophenyl	145	146·5	275	229—230
4-Chlorophenyl	Ethyl	137—138	175	—	—
,,	Phenyl	150	176—177	204—205	217
,,	4-Chlorophenyl	142	160	249	155
4-Bromophenyl	Methyl	133	199	—	—
,,	Ethyl	145—146	189—190	190	244
,,	Phenyl	160	200	255	216
4-Nitrophenyl	Methyl	206	233	—	—
,,	Phenyl	198—200	220	—	—
Phenyl	1-Naphthyl	—	183	—	160
4-Tolyl	,,	—	184	—	—
2-Tolyl	,,	—	176	—	—
4-Bromophenyl	,,	—	185	—	—
Phenyl	2-Naphthyl	—	191	—	—
4-Tolyl	,,	125	184	275	210
4-Bromophenyl	,,	183	202	278	254

$R^{(1)}$.	$R^{(4)}$.	Semicarbazide (Syn).	Thiobiazolone.
2-Tolyl	Methyl	158—159°	—
,,	Ethyl	130—131	—
,,	Phenyl	146—147	197
,,	2-Tolyl	148—149	—
,,	4-Tolyl	141—142	—
2-Chlorophenyl	Methyl	147	—
,,	Phenyl	156	171
2-Nitrophenyl	Methyl	201—202	—
,,	Ethyl	167—168	—
,,	Phenyl	185—186	—
2-Anisyl	Methyl	153	—
,,	Phenyl	150—151	—
3-Chlorophenyl	Methyl	171	—
,,	Phenyl	138—139	185—186
,,	3-Chlorophenyl	142	—
3-Bromophenyl	Methyl	127—128	—
,,	Phenyl	113	—
3-Nitrophenyl	Methyl	176—177	—
,,	Phenyl	164	223
2 : 4-Xylyl	Methyl	179—180	—
,,	Phenyl	149	158
2 : 4 : 5-Tribromophenyl	Methyl	206	—
,,	Phenyl	203	—
,,	4-Tolyl	201	—
1-Naphthyl	Methyl	195	—
,,	Ethyl	149	—
,,	Phenyl	(135) 220	224
,,	4-Tolyl	169	—
,,	1-Naphthyl	192	—
,,	2- ,,	179	233
2-Naphthyl	Methyl	209	153
,,	Ethyl	169	—
,,	Phenyl	202	199
,,	2-Tolyl	192	—
,,	4- ,,	195	—
,,	1-Naphthyl	207	—
,,	2- ,,	187	—

Methyl- and *ethyl-benzyloxythiocarbamides,* $NHR \cdot CS \cdot NH \cdot O \cdot CH_2Ph$, were prepared by mixing alcoholic solutions of methyl and ethyl thiocarbimides with α-benzylhydroxylamine; they melt at 87° and 67° respectively.   C. F. B.

Azonium Chromogens. III. Ethylnaphthaphenazonium and its Derivatives. By W. G. SCHAPOSCHNIKOFF (*Chem. Centr.*, 1898, ii, 919—920 ; from *J. Russ. Chem. Soc.*, 30, 546—553. Compare this vol., i, 431).—*Amidoethylnaphthaphenazonium,* prepared by condensing dichloroquinonedi-imine with β-naphthylethylamine in alcoholic solution, separates in silky, golden needles, is easily soluble in water and alcohol, forms almost insoluble double salts with the chlorides of zinc, mercury, gold, and platinum, and, with potassium hydroxide, yields the free base as a violet, crystalline precipitate.

Acetoethylisorosinduline, $C_{10}H_6 \lll {}^{N————}_{N\,EtCl} \ggg C_6H_3 \cdot NHAc$, prepared by the action of acetic anhydride on the preceding compound, crystallises in lustrous, green prisms. *Ethylnaphthaphenazonium* is obtained by diazotising amidoethylnaphthaphenazonium sulphate, or its acetyl derivative, dissolved in concentrated sulphuric acid, and then isolating it as the ferric chloride compound, $C_{18}H_{15}N_2Cl,FeCl_3$, which melts at 205°, is decomposed by alkali carbonates, forming ferric oxide and ethylnaphthaphenazonium carbonate, and gives a yellow, crystalline precipitate with hydrochloric acid. The base itself is easily soluble in water, slightly in alcohol and acetic acid, and forms a *platinochloride*, $(C_{18}H_{14}N_2)_2, H_2PtCl_6$, as an orange, crystalline powder insoluble in cold water. *Ethylrosinduline*, prepared by the action of ammonia in alcoholic solution on ethylnaphthaphenazonium, forms a *nitrate* which separates in orange crystals, is soluble in water, and forms a fluorescent solution in alcohol. The base is precipitated in golden scales by alkalis or ammonia. *Dimethylethylrosinduline*, prepared by treating ethylnaphthaphenazonium with dimethylamine, forms salts which, on boiling in aqueous solution with acids or mineral salts, lose the dimethylamine group and form *ethylrosindone*, $O \lll {}^{C_{10}H_5 \cdot N————}_{N\,Et} \ggg C_6H_4$.

This compound, obtained also by boiling ethylnaphthaphenazonium or its salts with sodium hydroxide, is a feeble base, crystallises in lustrous, yellow scales, melts at 180°, and is soluble in alcohol and benzene.

Dimethylethylisorosinduline, in which the dimethylamido-group is contained in the benzene nucleus, is prepared by condensing ethyl-β-naphthylamine with nitrosodimethylaniline hydrochloride; it is a violet pigment, and the *platinochloride*, $(C_{20}H_{19}N_3)_2, H_2PtCl_6$, is a dark green, crystalline powder. *Acetoethylnaphthaphenosafranine*, containing the NH_2-group in the nitrogen ring, the NHAc-group in the benzene ring, and both in the para-position with regard to the azine nitrogen, is prepared by the action of alcoholic ammonia on acetoethylisorosinduline in presence of air; it crystallises in green leaflets, and when dissolved in a 50 per cent. solution of sulphuric acid and boiled, yields *ethylnaphthaphenosafranine*, which crystallises from alcohol in small prisms with a metallic lustre, and is easily soluble in water and alcohol. The base is soluble in ether, and the *platinochloride*,

$$(C_{18}H_{16}N_4)_2, H_2PtCl_6,$$
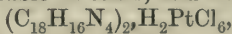
is a dark red, crystalline powder insoluble in water.

All these compounds are dyes. The replacement of the aromatic radicle of the quinquevalent azine nitrogen by a fatty group has no greater effect on the properties of the compound than that of the acid group in the various salts of the same compound, but the compounds in which the substituted group is in the benzene ring are very different in colour and properties to those in which the group is in the naphthalene ring.   E. W. W.

Constitution of the Azonium Compound from Benzil and Orthamidodiphenylamine. By FRIEDRICH KEHRMANN and W. WOULFSON (*Ber.*, 1899, **32**, 1042—1045).—In a footnote to an earlier

communication (*Ber.*, 1891, **24**, 1240), it was mentioned that from certain considerations it seemed probable that the azonium base obtained from benzil and orthamidodiphenylamine [phenylorthophenylenedi-amine] was in reality a tertiary alcohol, and that, on treating the azonium chloride with potassium hydroxide, a migration of the hydroxyl group had taken place from the azonium nitrogen to the neighbouring carbon atom of the ring. This view has now received support from the close similarity between the quinoxaline derivative formed by the condensation of benzoin and phenylorthophenylenediamine and the azonium base in question, the only difference being that, in one case, the red colour produced by alcoholic hydrochloric acid is permanent, whilst in the other it is merely temporary. If the formation of the azonium salt, however, is prevented, by converting the hydroxyl into an acetoxyl group by means of acetic anhydride, an *acetyl* compound which crystallises from benzene with benzene of crystallisation is produced; this, on treatment with alcoholic hydrochloric acid, gives a bluish-red coloration, permanent for months, and, on standing, deposits red crystals of the hydrochloride, a behaviour which is identical with that shown by the above mentioned benzoin condensation product.

<div align="right">J. F. T.</div>

Hydrolysis of Acid Amides. By IRA REMSEN (*Amer. Chem. J.*, 1899, **21**, 281—284).—In previous communications (Abstr., 1878, 405; 1879, 52; 1880, 257), attention has been drawn to the protective action of an ortho-substituent on alkylic groups in the benzene nucleus during oxidation with chromic anhydride. In a preliminary note (Abstr., 1897, i, 412), the protective influence of ortho-groups during the hydrolysis of substituted benzamides has also been noticed. The following abstract contains an account of experiments undertaken for the purpose of studying this protective influence more in detail.

<div align="right">J. J. S.</div>

Hydrolysis of Acid Amides. By E. EMMET REID (*Amer. Chem. J.*, 1899, **21**, 284—348. Compare preceding abstract, also Sudborough, Jackson, and Lloyd, Trans., 1897, **71**, 229).—The hydrolysis of substituted benzamides by dilute acids and alkalis has been studied by the aid of the equation, $K = 2\cdot3025/(A - B)t\cdot\log.\ (A - x/B - x\cdot B/A)$, where A and B represent the original concentrations of the acid (or alkali) and amide respectively, and $A - x$ and $B - x$, their concentrations after t minutes.

A weighed quantity of the amide was heated with acid of the required strength on a water-bath, kept vigorously boiling, the flask being fitted with a reflux condenser and a syphon for removing part of the liquid after given intervals. The portion thus removed was run into cold water, the amount of ammonium salt estimated by boiling with magnesium hydroxide and collecting the ammonia in standard acid; the unaltered amide was then determined by boiling the residue with concentrated sodium hydroxide and again receiving the ammonia in standard acid.

Preliminary experiments made with the three nitrobenzamides indicate that when hydrochloric acid is employed, the ortho-compound is hydrolysed much more slowly than the meta- and para-derivatives, the constants for the latter changing but little with the concentration

of the acid.   The ratio of the constants meta/para is approximately the same for both sulphuric and hydrochloric acids, the actual constants for sulphuric acid being those for hydrochloric × 0·45.   Alkalis gave large but decreasing constants and, when prepared by the addition of barium hydroxide to sodium or potassium sulphate solutions gave much lower results owing to the retarding action of the neutral salt present ; pure barium hydroxide gave higher results owing to the absence of neutral salt.

A few experiments on the influence of temperature on the reaction indicate that between 60° and 100, the values form a geometrical series.

The following values for the constant K have been obtained by the aid of 0·5769 N hydrochloric acid :

	Ortho.	Meta.	Para.
Benzamide .... $K.$ 0·0209			
Amidobenzamide.........	0·00178	0·01735	0·0198 ⎫ 0·0177 ⎭
Chlorobenzamide	0·00321	—	0·0179 ⎫ †0·0204 ⎬ †0·0196 ⎭
Iodobenzamide............	0·00106	—	—
Nitrobenzamide	0·00054	0·0196	0·0236 ⎫ †0·0256 ⎭
Toluamide.................	0·00222	0·0193	0·0175
Hydroxybenzamide	0·00437	—	—
Methoxybenzamide	0·0116	—	—
Ethoxybenzamide	0·0093	—	—
Bromobenzamide	—	0·0184 ⎫ †0·0210 ⎭	0·0146 ⎫ †0·0186 ⎬ †0·0173 ⎭

† These results were obtained when the concentration of the amide was half that employed in the other cases.

The results show that an ortho-substituent exerts a remarkable protective influence on the ·$CONH_2$-group.   With similar groups, the influence varies roughly with the weight of the group, but otherwise appears to depend more on the nature of the group than on its mass ; for example, the methyl group protects to a greater extent than does the heavier chlorine or methoxy-group.   The nitro-group is remarkable for its great protective power (compare Kellas, Abstr., 1898, i, 86).   Hydroxyl also protects to a greater extent than the methoxy- or ethoxy-group.

The results, in general, are in accord with those obtained by V. Meyer, Sudborough, Kellas, and others on the etherification of substituted benzoic acids, although the effect of the nature, rather than of the mass, of the substituent is brought more clearly into prominence.   J. J. S.

Action of Oxidising Agents on some Amides. By WILLIAM ŒCHSNER DE CONINCK (Compt. rend., 1899, 128, 503—505). Compare Abstr., 1898, 564, this vol., i, 243, 244, 420).—Phthalimide is decomposed at a somewhat high temperature by a mixture of potassium chromate solution and sulphuric acid, with liberation of carbonic

anhydride, but not of nitrogen. Potassium hydroxide and hydrogen peroxide decompose it very slowly, producing carbonic anhydride and ammonia.

Chromic mixture has very little action on succinamide, but partially decomposes glycocine and more readily attacks sarcosine. In no case is nitrogen liberated.

Formamide is violently attacked by potassium chromate solution and sulphuric acid, but nitrogen is not liberated ; alkaline hydrogen peroxide converts it into ammonia and carbonic anhydride. Acetamide yields the same products, but is much less readily attacked. Benzamide is only partially decomposed by the chromate and sulphuric acid ; nitrogen is not liberated, and a small quantity of benzonitrile is formed.

Formanilide is rapidly decomposed by chromic mixture, liberating carbonic anhydride and producing colouring matters. Acetanilide behaves in a similar way. C. H. B.

2-Chlorophenylthiocarbimide. By E. GROSCH (*Ber.*, 1899, 32, 1088—1089).—The compound described under this name by Hofmann (Abstr., 1880, 387) must have been the para-isomeride, for orthochloraniline will not unite with carbon bisulphide, except to form chlorophenylic chlorophenylthiocarbamate. On the other hand, orthochloraniline (4 mols.) reacts with carbonyl chloride (1 mol.) in benzene solution, the product being diorthochlorophenylthiocarbamide, which melts at 141°. If only 3 mols. of orthochloraniline are taken, the product is *orthochlorophenyl thiocarbimide*, $C_6H_4Cl\cdot N\dot{:}CS$; this boils at 248° and does not solidify in the cold ; with aniline, it yields an orthochlorodiphenylthiocarbamide identical with that obtained from phenylthiocarbimide and orthochloraniline. C. F. B.

Synthesis of Aromatic Carboxylic Acids. By LUDWIG GATTERMANN (*Ber.*, 1899, 32, 1116—1121).—The method formerly described by the author for preparing acid amides from aromatic hydrocarbons or phenol ethers (Abstr., 1890, 974) is best carried out as follows : dry hydrogen chloride is passed over strongly heated cyanuric acid contained in a hard glass tube, and the chloroformamide thus formed led into a reflux apparatus containing the hydrocarbon or phenol ether, carbon bisulphide, and finely powdered aluminium chloride, the temperature being maintained at 30—40°. On cooling, two layers form, the lower of which is separated and poured into ice cold water, when nearly the theoretical yield of the required acid amide is obtained. To hydrolyse this to the corresponding carboxylic acid, a modification of Bouveault's method (Abstr., 1893, ii, 541) is employed, which consists of adding sodium nitrite to a boiling solution of the amide in dilute sulphuric acid. By employing these methods, the author has prepared the following compounds.

[With PRENTICE.]—*Isodurene-6-carboxylic acid*, $C_6HMe_4\cdot COOH$, separates from light petroleum in colourless prisms and melts at 164—165°, whilst the *amide*, $C_{11}H_{15}NO$, crystallises from water in needles and melts at 141—142° ; in accordance with Victor Meyer's law, the acid does not yield an ethereal salt when boiled for 3 hours with 3 per cent. alcoholic hydrogen chloride.

When durene is treated by the new method, it gives rise to a mixture of the amides of durenecarboxylic, isodurenecarboxylic, and prehnitolcarboxylic acids; durenecarboxylic acid, however, can readily be obtained pure by treating the hydrocarbon with chloroformamide in presence of aluminium chloride at 0° (compare Abstr., 1887, 569, and 1888, 574), and hydrolysing the resulting amide with nitrous acid; it melts at 177°, not at 112° as formerly stated.

[With KJELLBOM.]—*Paradiphenylbenzamide*, $C_6H_4Ph \cdot CO \cdot NH_2$, crystallises from acetic acid in colourless needles and melts at 222—223°, whilst *parapropoxybenzamide*, $C_{10}H_{13}NO_2$, separates from dilute alcohol in colourless needles and melts at 154°.

[With EUGEN OBERLÄNDER.]—The *amide*, $OMe \cdot C_6H_2MePr_\beta \cdot CO \cdot NH_2$, prepared from carvacrylic methylic ether, crystallises from dilute alcohol in colourless needles, melts at 163—164°, and on hydrolysis yields the corresponding *acid*, $C_{12}H_{16}O_3$, which forms colourless, lustrous needles and melts at 154—155°; the *amide*, $C_{13}H_{19}NO_2$, prepared form carvacrylic ethylic ether, has similar properties and melts at 133—134°, whilst the *acid*, $C_{13}H_{18}O_3$, prepared from it crystallises from water in colourless needles and melts at 133°.

[With J. A. RÖLOFSEN.]—*Orthochloroparanisamide*,

$$OMe \cdot C_6H_3Cl \cdot CO \cdot NH_2,$$

prepared from orthochloranisoil, crystallises from water in colourless needles and melts at 193°, whilst *orthobromoparanisamide* has similar properties and melts at 185°.

From the examples given, it appears that, in the treatment of phenolic ethers by the above method, the $\cdot CO \cdot NH_2$-radicle always takes up a para-position with regard to the alkyloxy-radicle.　　　　W. A. D.

Action of Aniline and Phenylcarbimide on Ketonic Acids of the $C_nH_{2n-10}O_3$ Series.

By TIMOTHÉE KLOBB (*Bull. Soc. Chim.*, 1898, [iii], **19**, 389—399).—Haller has shown that phenylcarbimide reacts with carboxylic acids to form acid anhydrides or anilides, according to the temperature employed. The author has applied this reaction to certain γ-ketonic acids, and obtained some new compounds derived from the anilides by the elimination of water.

When β-benzoylpropionic acid is heated with phenylcarbimide at a temperature not exceeding 90—100°, a yellow, viscous, odorous substance is obtained which is in all probability the true *anhydride* of the acid, since it is wholly converted into the latter by prolonged boiling with water, and is quite different from the phenylcrotonolactone which Fittig (Abstr., 1898, i, 196) obtained by the action of acetic anhydride on β-benzoylpropionic acid. If, however, the heating is continued until a temperature of 200° is reached, the principal product of the reaction is a *substance* crystallising in slender, yellow needles melting at 195°, whilst a variable quantity of the anilide is also formed. If 1 mol. of β-benzoylpropionic acid is heated with 2 mols. of phenylcarbimide, the yellow substance is exclusively formed, whilst if aniline is employed instead of phenylcarbimide, the anilide is the principal product. β-Benzoylpropionanilide, which has previously been obtained by Biedermann, crystallises from boiling benzene in thin leaflets, and from alcohol in large plates which melt

at 145° and are very soluble in alcohol, acetic acid, and chloroform, insoluble in light petroleum; when heated with fuming hydrochloric acid at 100°, it is quantitatively converted into aniline and β-benzoylpropionic acid. The yellow substance melting at 195° has the molecular formula $C_{32}H_{26}N_2O_2$, and is derived from 2 mols. of the anilide of β-benzoylpropionic acid by elimination of 2 mols. of water; the constitution $NHPh \cdot CO \cdot CH_2 \cdot CH_2 \cdot CPh:C {<} \begin{smallmatrix} CO \cdot NPh \\ CH:CPh \end{smallmatrix}$ is suggested as being more probable than the symmetrical formula,

$$NHPh \cdot CO \cdot C {<} \begin{smallmatrix} CPh \cdot CH_2 \\ CH_2 \cdot CPh \end{smallmatrix} {>} C \cdot CO \cdot NHPh.$$
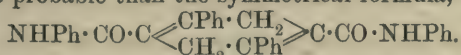
The latter is inconsistent with the instability of the compound, as shown by its resolution into aniline and β-benzoylpropionic acid by the action of fuming hydrochloric acid at 150°, whilst the former explains the fact that no analogous compound is obtained from β-benzoyl-α-methylpropionic acid, in which there is only 1 atom of hydrogen available in the α-position. It is very soluble in cold benzene, soluble in boiling chloroform, ether, and acetone, scarcely soluble in cold alcohol; it dissolves in concentrated sulphuric acid, from which it is reprecipitated unchanged by addition of water. When dissolved in alcoholic potash, the solution absorbs oxygen from the air, becomes brown, and, after some days, evolves an odour of phenylcarbamine, and contains a white, crystalline *substance* melting at about 245°.

β-Benzoyl-α-methylpropionic acid, when heated at 100° with phenylcarbimide, yields a pale green, viscous substance of agreeable aromatic odour, which is doubtless the *anhydride* of the acid, but if the heating be continued up to a temperature of 200°, the principal product of the reaction is 1:5-*diphenyl-3-methylpyrrolone*, $CHMe {<} \begin{smallmatrix} CO \cdot NPh \\ CH:CPh \end{smallmatrix}$; this crystallises in colourless, monoclinic prisms, melts at 128—130°, sublimes without decomposition, and is very soluble in alcohol, acetic acid, and benzene. It does not absorb oxygen in presence of alcoholic potash, is not acted on by acetic anhydride at 150°, and is resolved by heating with fuming hydrochloric acid at 100° into aniline and β-benzoyl-α-methylpropionic acid. The *anilide* of the latter, which is obtained by the direct action of aniline on the acid, crystallises from boiling benzene in white needles melting at 188—190°, and subliming without decomposition. N. L.

Propiophenoneorthocarboxylic Acid and Benzyl Methyl Ketone-orthocarboxylic Acid. By JACOB GOTTLIEB (*Ber.*, 1899, **32**, 958—967. Compare Abstr., 1878, 735).—Ethylidenephthalide is most readily obtained by heating together perfectly dry sodium propionate, phthalic anhydride, and propionic anhydride for 1·5—2 hours at 160—170°; the mixture is then warmed with water, and finally extracted with dilute acid, when the phthalide is left as a yellowish-red, crystalline mass, the yield being 88 per cent. of the propionic anhydride employed. As the phthalide, when kept for some time, becomes resinous, it is advisable to convert it at once into ortho-

propiophenonecarboxylic acid by warming with sodium hydroxide, and then precipitating with hydrochloric acid.

When warmed with phenylhydrazine, propiophenonecarboxylic acid yields 3-*phenyl*-1-*ethylphthalazone*, $C_6H_4{<}{\stackrel{CEt:N}{\underset{CO-NPh}{}}}$, which crystallises from alcohol in short, dark-yellow prisms melting at 102° and readily soluble in organic solvents.

Glycocine converts the acid into *ethylidenephthalimidylacetic* acid, $C_6H_4{<}{\stackrel{C(:CHMe)}{\underset{CO-}{}}}{>}N{\cdot}CH_2{\cdot}COOH$ (compare Abstr., 1897, i, 59), which crystallises from acetic acid or dilute alcohol in prisms melting at 205—207°; its *silver* salt, $C_{12}H_{10}NO_3Ag$, forms a white, crystalline precipitate.

Ethylphthalide, $C_6H_4{<}{\stackrel{CHEt}{\underset{CO-}{}}}{>}O$, obtained when the orthocarboxylic acid is reduced in alkaline solution with sodium amalgam, solidifies to a yellow, crystalline mass melting at 12° and distilling at 291° under 760 mm. pressure. The hydroxy-acid corresponding with this lactone has not been obtained in a pure form. *Ethylnitrophthalide*, $C_{10}H_9N_4O$, crystallises from alcohol in long, yellowish prisms melting and decomposing at 63—64°; the nitro-group is probably in the meta-position to the ethyl group.

Orthopropylbenzoic acid is readily obtained when ethylphthalide is boiled for 96 hours in a reflux apparatus with red phosphorus and hydriodic acid boiling at 127°. The *silver* salt, $C_{10}H_{11}O_2Ag$; *copper* salt, $(C_{10}H_{11}O_2)_2Cu + 4H_2O$; *acid chloride*, $C_6H_4Pr{\cdot}COCl$, boiling at 236°; *anilide*, $C_6H_4Pr{\cdot}CONHPh$, crystallising in prismatic plates and melting at 108—109°; *ureide*, $C_6H_4Pr{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, melting at 171—172°; *amide*, $C_6H_4Pr{\cdot}CO{\cdot}NH_2$, melting at 127—128°; *ethylic* salt boiling at 244—247° under 785 mm. pressure, and of sp. gr. 1·003 at 15°/15°; and *nitrile*, boiling at 227—229° under 758 mm. pressure, have all been prepared. The *thioamide*, $C_6H_4Pr{\cdot}CS{\cdot}NH_2$, obtained by the action of alcoholic ammonium sulphide on the nitrile at 100°, crystallises from its aqueous solution in long needles melting at 53—54°. *Orthopropylaniline*, obtained by the action of sodium hypobromite on orthopropylbenzamide, is a colourless liquid boiling at 222—224°.

Nitrorthopropylbenzoic acid, $NO_2{\cdot}C_6H_3Pr{\cdot}COOH$, melts at 116—118°; when reduced, it yields an *amido*-acid which crystallises from water in needles melting at 157—158°.

A better yield of methylisocoumarin (Abstr., 1893, i, 228) is obtained when ψ-diacetylorthobenzylic cyanide is boiled with aqueous phosphoric acid instead of with acetic and hydrochloric acids; when boiled with potassium hydroxide solution, it is converted into *benzyl methyl ketone-orthocarboxylic acid*, $COMe{\cdot}CH_2{\cdot}C_6H_4{\cdot}COOH$; this forms broad, long needles, melts at 118—119°, and is soluble in the ordinary solvents. Its *silver* salt crystallises in slender, glistening needles, and its *copper* salt in dark green, glistening, anhydrous needles. Its *oxime* crystallises from 50 per cent. alcohol in slightly reddish plates melting at 162°, and when heated at 162° for 20 minutes is con-

verted into an *anhydride* which crystallises from acetone in needles melting at 171—173°. The *anhydride* of the *phenylhydrazone*,

$C_6H_4 \begin{cases} CH_2 \cdot CMe \vdots N \\ CO \qquad\qquad NPh \end{cases}$, crystallises from alcohol in quadratic prisms

melting at 198—199°, and is sparingly soluble in alcohol, ether, benzene, or acetic acid.

The orthocarboxylic acid readily reacts with glycocine at 160°, yielding a compound, $C_{12}H_{11}NO_2$, which melts and decomposes at 220°.

Methylisocoumarin dibromide crystallises from light petroleum in long prisms melting and decomposing at 64—66°.   J. J. S.

Action of Isopropylic Iodide on Phthalic Anhydride in Presence of Zinc Dust : Purification of Propylphthalide. By PIETRO GUCCI (*Gazzetta*, 1898, **28**, ii, 501—508).—On warming a mixture of zinc dust, isopropylic iodide, and phthalic anhydride, a vigorous action takes place, large quantities of inflammable gas being evolved and an oil produced ; the latter, when distilled under the ordinary pressure, yields propylene and phthalic anhydride, and, on hydrolysis, gives rise to isopropylic alcohol, phthalic acid, isopropylphthalide, and the isobutyrylbenzoic acid obtained by Roser (Abstr., 1885, 267), by boiling isopropylidenephthalide with potash. From this, it is inferred that the products of the reaction

are isopropylic phthalate and isopropylphthalide, $C_6H_4 \begin{cases} CHPr^\beta \\ CO \end{cases} O$;

the latter, after drying in ethereal solution by means of calcium chloride, and subsequently heating at 150° in a vacuum, boils at 225—229° under 160 mm. pressure.

When purified by this method, the normal propylphthalide already obtained by the author (Abstr., 1898, i, 665) boils at 230—234° under the same pressure.   T. H. P.

Thiofluorescein and Some Derivatives of the Phthaleins. By LUDWIG GATTERMANN (*Ber.*, 1899, **32**, 1127—1135).—[With ROBERT GANZERT].—Although, as stated by von Baeyer, fluorescein chloride is not converted into fluorescein by heating with alcoholic potash, it readily gives rise to thiofluorescein when heated with concentrated alcoholic potassium hydrosulphide for half an hour on the water-bath ; thus obtained, thiofluorescein is a grey, amorphous powder, which is nearly insoluble in the ordinary solvents, does not melt below 300°, and dissolves in aqueous alkalis and ammonia with a more intensely blue coloration than that given by fluorescein under similar conditions. The colour, however, disappears when the alkaline solution is exposed for a long period to the air, owing to oxidation occurring, and is rapidly removed by warming with zinc dust ; the colourless solution obtained in the latter case, however, again becomes blue when exposed to the air.

[With G. DE RIDDER].—When fluorescein chloride, dissolved in alcohol, is heated for half an hour with thiophenol and potassium hydroxide, it gives rise to the *phenyl* derivative,

$$O \begin{cases} C_6H_3(SPh) \\ C_6H_3(SPh) \end{cases} C \begin{cases} C_6H_4 \\ O \end{cases} CO,$$
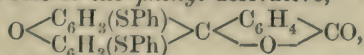
of thiofluorescein, which crystallises from glacial acetic acid in colourless needles and melts at 197—198°.

[WITH R. BERENDES].—The corresponding *orthotolyl* derivative, $C_{34}H_{24}S_2O_3$, prepared from orthothiocresol, crystallises from the same solvent in colourless prisms and melts at 200—201°. The isomeric *thiofluorescein ethers*, $C_{36}H_{28}S_2O_5$, prepared from orthethoxythiophenol and 4-methoxymetathiocresol, crystallise from glacial acetic acid in flesh-coloured needles and melt respectively at 187° and 144—145°.

[With F. BAMBERG].—The *compound*, $C_{34}H_{24}S_2O_5$, obtained from thioguaiacol, crystallises in rose-coloured needles and melts at 212—213°.

Dinitrophenolphthalein (Hall, Proc., 1893, 14 ; Errera and Berté, Abstr., 1896, i, 564) is conveniently prepared by carefully adding a mixture of concentrated nitric and sulphuric acids to a solution of phenolphthalein in glacial acetic acid cooled by ice, the temperature not being allowed to rise above 20° ; when heated with an excess of alcoholic potassium hydrosulphide, it is converted into *diamidophenolphthalein*, $C_{20}H_{16}N_2O_4$, which can also be obtained by reducing the dinitro-compound with stannous chloride, and is a greyish, crystalline powder. Alkaline solutions of the base have a deep blue colour, but soon become decolorised when exposed to the air.

[With ROBERT GANZERT].—When fluorescein is boiled for a short period with phenylhydrazine, it gives rise to the *phenylhydrazide*,
$$O{<}{C_6H_3(OH) \atop C_6H_3(OH)}{>}C{<}{C_6H_4 \atop N_2HPh}{>}CO,$$
which separates from ether and glacial acetic acid in colourless crystals, and dissolves in alkali giving a colourless, fluorescent solution ; the *phenylhydrazide*, $C_{26}H_{16}N_2Cl_2O_2$, of fluorescein chloride, prepared by boiling the latter with phenylhydrazine, forms colourless needles, melts at 265°, and is insoluble in alkalis ; *phenolphthalein phenylhydrazide*, $C_{26}H_{20}N_2O_3$, crystallises from glacial acetic acid in colourless needles, and dissolves in alkalis, giving a colourless solution.

[With CARL G. OEHMICHEN].—When fluorescein phenylhydrazide is heated with methylic iodide and an alcoholic solution of potassium hydroxide for an hour, it gives rise to the *dimethylic ether*,
$$O{<}{C_6H_3(OMe) \atop C_6H_3(OMe)}{>}C{<}{C_6H_4 \atop N_2HPh}{>}CO,$$
which crystallises from hot glacial acetic acid on adding water in colourless, silky needles and melts at 227—228° ; the corresponding *diethylic ether*, $C_{30}H_{26}N_2O_4$, forms slightly yellow-coloured, lustrous needles, and melts at 247—248°. The *dimethylic ether*, $C_{28}H_{24}N_2O_3$, of phenolphthaleinphenylhydrazide crystallises in yellow needles and melts at 228°, whilst the *diethyl* derivative, $C_{30}H_{28}N_2O_3$, forms colourless needles and melts at 241—242°.
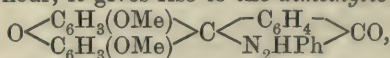
When fluorescein is heated for a short time with concentrated hydrochloric acid at 180°, it gives rise to brownish-red plates of the *additive* compound, $C_{20}H_{12}O_5,HCl$, which is easily resolved by alkalis into its components, and is analogous to the additive compound obtained by von Baeyer from fluorescein and sulphuric acid (*Annalen*, 1862, 123, 27). W. A. D.

Synthesis of Uvitic Acid from Pyruvic Acid. By LUDWIG WOLFF [and F. HEIP] (*Annalen*, 1899, 305, 125—153).—The change

by which pyruvic acid is converted into uvitic (symmetrical methylisophthalic) acid, first observed by Finck, has not yet been adequately explained. The author has isolated an intermediate product, methyldihydrotrimesic acid, $C_{10}H_{10}O_6$, and it is the elimination of hydrogen and carbonic anhydride from this substance which gives rise to uvitic acid, the two stages being represented by the equations I. $4C_3H_4O_3 = C_{10}H_{10}O_6 + C_2H_2O_4 + 2H_2O$. II. $C_{10}H_{10}O_6 = C_9H_8O_4 + CO_2 + H_2$. It is probable that 2 molecules of pyruvic acid first undergo condensation to parapyruvic acid,

$$COOH \cdot CMe(OH) \cdot CH_2 \cdot CO \cdot COOH,$$
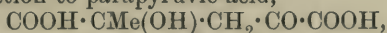
(this vol., i, 483), 2 molecules of which then lose oxalic acid and water, yielding methyldihydrotrimesic acid.

Methyldihydrotrimesic (1 *methyl*-$\Delta^{2,4}$-*dihydrobenzene*-1 : 3 : 5-*tricarboxylic*) *acid*, $COOH \cdot CMe \underset{CH_2 \cdot C(COOH)}{\overset{CH : C(COOH)}{<}} > CH$, prepared by heating pyruvic acid with aqueous soda during 2 hours in boiling water, crystallises from dilute alcohol in lustrous leaflets containing $1H_2O$ which is lost at 100°; it loses carbonic anhydride at 195°, and melts at 245—250°. The acid reduces Fehling's solution and potassium permanganate; it does not yield an additive compound with bromine, but is easily reduced by sodium amalgam, yielding methyltetrahydrotrimesic acid. Boiling baryta converts it slowly into uvitic acid. The *barium* salt contains $8\frac{1}{2}H_2O$, and is slowly decomposed by boiling water; the *methylic* salt, which crystallises from a mixture of ether and petroleum in small leaflets, sinters at 72° and melts at 76°.

When methyldihydrotrimesic acid is heated at 200—240° until carbonic anhydride ceases to be evolved, five hydrogenised isophthalic acids, in addition to uvitic acid, are produced. $\Delta^{2,4}$-*Dihydrouvitic acid*, $CHMe \underset{CH_2 \cdot C(COOH)}{\overset{CH : C(COOH)}{<}} > CH$, occurs in the boiling water extract of the fused methyldihydrotrimesic acid, and crystallises from hot water in small prisms melting at 235—236°; the *barium* and *calcium* salts contain $2\frac{1}{2}H_2O$ and $3\frac{1}{2}H_2O$ respectively. Δ^4-*Tetrahydrouvitic acid*, $CHMe \underset{CH_2 - C(COOH)}{\overset{CH_2 \cdot CH(COOH)}{<}} > CH$, dissolves more sparingly in water than the following three isomerides, and remains in association with dihydrouvitic acid when the fused methyldihydrotrimesic acid has been extracted with cold water; it crystallises from water in small plates melting at 223—224°, and is formed when dihydrouvitic acid is reduced with sodium amalgam. α-*Tetrahydrouvitic acid* crystallises from hot water in large plates and melts at 179—180°. β-*Tetrahydrouvitic acid* melts at 168—169°; it crystallises from water in long needles, and from dilute methylic alcohol in stout prisms. γ-*Tetrahydrouvitic acid* forms a colourless syrup, and is probably identical with uvitonic acid, obtained by Finck as a bye-product in the preparation of uvitic acid; the *calcium* salt contains $1H_2O$.

Methyltetrahydrotrimesic acid, $COOH \cdot CMe \underset{CH_2 - C(COOH)}{\overset{CH_2 \cdot CH(COOH)}{<}} > CH$, prepared by reducing methyldihydrotrimesic acid in alkaline solution with sodium amalgam, melts at 220—222°, slowly evolving gas; it crystallises from water in slender needles, and sometimes contains

1H$_2$O. Unlike methyldihydrotrimesic acid, it is indifferent towards boiling water, and yields only a small proportion of uvitic acid under the influence of concentrated sulphuric acid. The tetrahydro-acid reduces potassium permanganate, and is also oxidised by heated Fehling's solution ; elimination of carbonic anhydride at 230—240° converts it into α-tetrahydrouvitic acid.

When methyldihydrotrimesic acid is oxidised with cold potassium permanganate, uvitic acid is produced, the hot agent giving rise to trimesic acid ; uvitic acid is also formed when the oxidation is carried out with ferric sulphate or nitric acid.   M. O. F.

Action of Zinc and Ethylic Chloracetate on Ethylic Formate. Synthesis of Alkylic Trimesates. By SERGIUS N. REFORMATSKY (*Chem. Centr.*, 1898, ii, 472—473 ; from *J. Russ. Chem. Soc.*, 1898, **30**, 280—292).—Ethylic trimesate, prepared by the action of ethylic chloracetate, or, better, bromacetate, on ethylic formate, separates from benzene in yellowish crystals, melts at 133·5—134·5°, is soluble in hot alcohol, ether, or acetic acid, and insoluble in water. Molecular weight determinations by Raoult's method gave unsatisfactory results. Trimesic acid forms delicate, white, hair-like crystals, melts above 320°, is easily soluble in alcohol and hot water, and slightly in cold water, 2·69 per cent. being dissolved by water at 22·5° and 0·38 at 16°. The results obtained by titrating with barium hydroxide solution were too high. Methylic trimesate melts at 142·5° (compare Piutti, Abstr., 1887, 587). Several of the metallic salts of trimesic acid are described, amongst which the characteristic barium salt forms slender, hair-like crystals containing 4H$_2$O, and the silver salt forms a flocculent, insoluble mass, which, on burning, swells like mercury thiocyanate. Ethylic trimesate is not formed by the action of zinc chloride on a mixture of ethylic acetate and ethylic formate.   E. W. W.

Action of Sulphanilic Acid on Chloranil [Tetrachloroquinone] in Presence of Potash. By H. IMBERT and J. PAGÈS (*Bull. Soc. Chim.*, 1898, [iii], **19**, 575—576).—Sulphanilic acid has no action on tetrachloroquinone in presence of water alone, but if solid potash is gradually added to a boiling solution of potassium sulphanilate (2 mols.) and tetrachloroquinone (1 mol.) and the brown mass thus produced extracted with boiling water, a *compound* is obtained which has the formula $C_6Cl_2O_2(NH \cdot C_6H_4 \cdot SO_3K)_2$. This substance crystallises in long, yellow needles which dissolve slightly in cold, much more readily in hot, water forming a greenish-brown solution which yields a brown precipitate with barium salts and also, on heating, with lead salts, but is not affected by salts of silver, mercury, or copper. Soda may be used instead of potash in the preparation of the new compound, and a similar reaction occurs with tetrabromoquinone.   N. L.

Replacement of the Diazo-group by the Sulphinic Radicle. By LUDWIG GATTERMANN (*Ber.*, 1899, **32**, 1136—1159).—When a well-cooled aqueous solution of a diazo-sulphate containing an excess of sulphuric acid is saturated with sulphurous anhydride, and is subsequently surrounded by ice and gradually decomposed by adding copper-powder until no more nitrogen is evolved, the diazo-group is

replaced almost quantitatively by the sulphinic radicle SO_2H; the sulphinic acid formed, according to its solubility in water, is isolated by extracting either the aqueous solution or the copper precipitate with ether, and is purified by dissolving in alkali, subsequently acidifying, again extracting with ether, and finally crystallising from water. Diazo-chlorides can also be employed in preparing sulphinic acids by this method, but in most cases the yield is smaller than with the corresponding sulphates. In some cases, notably with the naphthylamines, the method can profitably be modified by carefully adding the solution of the diazo-salt to the copper powder suspended in a saturated aqueous solution of sulphurous acid.

The decomposition probably takes place in three stages, as follows : (I) $R\cdot N_2\cdot SO_4H + H_2SO_3 = R\cdot N_2\cdot SO_3H + H_2SO_4$; (II) $R\cdot N_2\cdot SO_3H - O = R\cdot N_2\cdot SO_2H$; (III) $R\cdot N_2\cdot SO_2H = N_2 + R\cdot SO_2H$. Quantitative determinations of the amount of copper passing into solution, as well as of the sulphuric acid formed, indicate that the reduction in equation II is effected by the copper powder, and not by the sulphurous acid employed.

The author cites a large number of examples of the application of the method, showing that, in nearly all cases, the yield is quantitative, and describes the following new compounds. Metaxylenesulphinic acid, $C_8H_9\cdot SO_2H$, crystallises from water in long, colourless needles and melts at 77—78°, not at 50° as stated by Jacobsen, whilst ψ-cumenesulphinic acid, $C_9H_{11}\cdot SO_2H$, melts at 107—108°, and not at 98° (Radloff, Abstr., 1878, 414), parachlorobenzenesulphinic acid at 93—94°, not at 88—89° (Otto and Brunner, *Annalen*, 143, 113), and parabromobenzenesulphinic acid at 114—115°, not at 103° (König, Abstr., 1892, 1091). *Orthanisoilsulphinic acid*, $C_7H_7O\cdot SO_2H$, crystallises from water in stout, colourless needles, melts at 98—99°, and, when treated with nitrous acid (compare Königs, Abstr., 1878, 573), yields the *compound* $(OMe\cdot C_6H_4\cdot SO_2)_2N\cdot OH$, which separates from alcohol in colourless, lustrous needles, and melts at 183—184°; *orthophenetoilsulphinic acid*, $C_8H_9O\cdot SO_2H$, crystallises from water in stout needles and melts at 91—92°; *paranisoilsulphinic acid* separates in long, lustrous needles and melts at 97—98°, whilst *paraphenetoilsulphinic acid* forms nacreous plates, melts at 104°, and yields, with nitrous acid, the compound $C_{16}H_{19}NS_2O_7$, which crystallises from alcohol in colourless needles and melts at 161°. *Methoxytoluenesulphinic acid* [$CH_3 : SO_2H : OMe = 1 : 3 : 4$] forms long, colourless needles and melts at 97°; *orthocarboxybenzenesulphinic acid*, $COOH\cdot C_6H_4\cdot SO_2H$, crystallises from glacial acetic acid or dilute alcohol in aggregates of needles, melts at 125°, and yields " saccharin " when heated with hydroxylamine for 3 hours at 100°; *metacarboxybenzenesulphinic acid* crystallises from alcohol in stout prisms and melts at 197—198°. *Sodium naphthalene-1-sulphin-4-sulphonate*, $SO_2H\cdot C_{10}H_6\cdot SO_3Na$, crystallises from water in small, colourless plates, whilst the *acid*, $C_{10}H_8S_2O_5$, forms lustrous, asbestos-like needles; *sodium naphthalene-1-sulphin-2-sulphonate*, $SO_2H\cdot C_{10}H_6\cdot SO_3Na + H_2O$, separates from water in yellowish crystals, whilst *disodium naphthalene-2-sulphin-4 : 1'-disulphonate*, $SO_2H\cdot C_{10}H_5(SO_3Na)_2 + H_2O$, crystallises from water, on adding alcohol, in colourless needles.

The following mercaptans have been prepared by reducing the corresponding sulphinic acids. *Metaxylylic mercaptan*, $C_6H_3Me_2 \cdot SH$, is a disagreeably smelling liquid which boils at 207—208°; *paraxylylic mercaptan* boils at 205—206°, orthomethoxythiophenol at 218—219°, and its *methylic ether*, $OMe \cdot C_6H_4 \cdot SMe$, at 237°; the *bisulphide*, $S_2(C_6H_4 \cdot OMe)_2$, prepared by adding finely powdered iodine to a solution of orthomethoxythiophenol in 10 per cent. caustic soda, crystallises from alcohol in lustrous, colourless needles and melts at 119—120°. *Orthethoxythiophenol*, $C_8H_{10}SO$, boils at 226—227°, and its *ethylic ether*, $C_{10}H_{14}SO$, at 248—250°, whilst the *bisulphide*, $C_{16}H_{18}S_2O_2$, crystallises from alcohol in stout needles and melts at 89—90°. *Paramethoxythiophenol* boils at 227°, its *methylic ether*, $C_8H_{10}SO$, at 239—240°, whilst the *bisulphide*, $C_{14}H_{14}S_2O_2$, melts at 44—45°; *parethoxythiophenol* boils at 238°, its *ethylic ether* at 259—260°, whilst the *bisulphide* forms lustrous needles and melts at 48—49°. *Methoxythiocresol* [$CH_3 : SH : OMe = 1 : 3 : 4$] boils at 244—245°; its *methylic ether* crystallises from alcohol in long, colourless needles and melts at 31·5°, whilst the *bisulphide* forms lustrous plates and melts at 64·5°.

When orthocarboxybenzenesulphinic acid is reduced with zinc dust and hydrochloric acid, it forms a mixture of thiosalicylic acid, $SH \cdot C_6H_4 \cdot COOH$ (Gräbe and Aulich, German Patent 69073; List and Stein, Abstr., 1898, i, 584), and dithiosalicylic acid, $S_2(C_6H_4 \cdot COOH)_2$; the *sodium* salt, $C_7H_5SNaO_2$, of the former crystallises in large, yellowish plates, whilst the *methylic* salt, $COOMe \cdot C_6H_4 \cdot SH$, is a colourless oil which boils at 252°. Dithiosalicylic acid, prepared by adding orthocarboxybenzenesulphinic acid dissolved in water to a hot solution of stannous chloride in concentrated hydrochloric acid, crystallises from alcohol in prisms and melts at 289°. Metacarboxybenzenesulphinic acid, when reduced with zinc dust and hydrochloric acid, yields the so-called " dithio-oxybenzoic acid " (dimetacarboxyphenylic bisulphide), $S_2(C_6H_4 \cdot COOH)_2$.

Sodium 1-thionaphthol-4-sulphonate, $C_{10}H_7S_2O_3Na$, prepared by reducing the corresponding sulphinic acid with tin and hydrochloric acid, crystallises from water in yellowish needles; when the reduction is carried out in concentrated solution, the *tin* salt, $(SO_3Na \cdot C_{10}H_6 \cdot S)_2Sn$, separates in yellow plates. The *tin* derivative, $C_{20}H_{12}S_4O_6Na_2Sn$, of sodium 1-thionaphthol-2-sulphonate is similarly obtained from naphthalene-1-sulphin-2-sulphonic acid, and crystallises from water in yellow needles. *Sodium 2-thionaphthol-4 : 1′-disulphonate*, $C_{10}H_6S_3O_6Na_2$, was also prepared.

The following sulphonic acids were obtained by oxidising the corresponding sulphinic derivatives with alkaline potassium permanganate. *Potassium orthanisoilsulphonate*, $C_7H_7SO_4K$, crystallises from absolute alcohol; the corresponding amide, $C_7H_9NSO_3$, melts at 169—170°, whilst the *anilide*, $C_{13}H_{13}NSO_3$, crystallises from alcohol in lustrous plates and melts at 161°. *Potassium orthophenetoilsulphonate*, $C_8H_9SO_4K$, forms lustrous needles; the corresponding *chloride*, nacreous plates melting at 65—66°; the *amide*, long needles melting at 163° (compare Lagai, Abstr., 1892, 1089); the *anilide*, large plates melting at 158°, and the *phenylhydrazide*, silky needles which melt at 132—133°. *Potassium paranisoilsulphonate*, $C_7H_7SO_4K$, crystallises from alcohol

in sheaf-like aggregates of needles ; the corresponding *amide* melts at 116°, and the *anilide* at 110—111° ; the properties of the corresponding phenetoil derivatives are those given by Lagai (*loc. cit.*). *Potassium methoxytoluenesulphonate*, $C_8H_9SO_4K$ [$CH_3 : SO_3K : OCH_3 = 1 : 3 : 4$], forms lustrous plates, the *chloride* crystallises from light petroleum in flattened needles, and melts at 67—67·5° ; the *amide* separates from alcohol in silky needles and melts at 138°, whilst the *anilide* melts at 163°. 1 : 4-Naphthalenedisulphonic acid is more easily prepared by oxidising naphthalene-1-sulphin-4-sulphonic acid than by Armstrong and Wynne's method (Proc., 1893, 166); the *amide*, $C_{10}H_{10}N_2S_2O_4$, crystallises from dilute alcohol in needles and melts at 273°, whilst the *anilide*, $C_{22}H_{18}N_2S_2O_4$, forms leaflets and melts at 179°.

When sodium hydrogen 1 : 4-naphthalenedisulphonate is nitrated in sulphuric acid solution and the nitro-derivative reduced by stannous chloride, *sodium hydrogen amidonaphthalenedisulphonate*, $SO_3H \cdot C_{10}H_5(NH_2) \cdot SO_3Na + 1\frac{1}{2}H_2O$ [$SO_3H : SO_3Na : NH_2 = 1 : 4 : 1'$], is obtained in brownish cubes, which are sparingly soluble in water ; that the amido-group is in the α-position is shown by the sodium salt yielding α-naphthylamine when reduced by sodium amalgam. *Naphthalene*-1 : 4 : 1'-*trisulphonic chloride* crystallises in beautiful needles and melts at 156—157° ; *sodium* 1' : 1-*naphthasultone*-4-*sulphonate*, $C_{10}H_5S_2O_6Na + \frac{1}{2}H_2O$, obtained on diazotising the corresponding sodium hydrogen amidonaphthalenedisulphonate and boiling with water, crystallises in beautiful, efflorescent needles, and, on reduction, yields α-naphthol. *Trisodium naphthalene*-2 : 4 : 1'-*trisulphonate*, $C_{10}H_5S_3O_9Na_3$, prepared from naphthalene-2-sulphin-4 : 1'-disulphonic acid, crystallises from alcohol in colourless needles, whilst the corresponding *chloride*, $C_{10}H_5S_3Cl_3O_6$, forms well-defined crystals and melts at 146°.   W. A. D.

Etard's Reaction. By MAX WEILER (*Ber.*, 1899, **32**, 1050—1056). —Paraditolyl, diphenylmethane, paratolylphenylmethane, or dibenzyl (1 mol.) was dissolved in carbon bisulphide and treated with a solution of chromyl chloride (2 mols.) in the same solvent, added in successive small portions at the ordinary temperature (compare Etard, Abstr., 1881, 581); the carbon bisulphide solution and the chromate precipitate were then worked up separately, the latter being decomposed with water. It was found that the chromyl chloride acted to some extent as a chlorinating, although mainly as an oxidising, agent.

Diphenylmethane yields benzophenone as sole product.

Paratolylphenylmethane yields phenyl paratolyl ketone together with some parabenzylbenzaldehyde and chlorotolylphenylmethane, $CH_2Ph \cdot C_6H_4 \cdot CH_2Cl$.

Paraditolyl yields 4'-*tolyl*-4-*benzaldehyde*, $C_6H_4Me \cdot C_6H_4 \cdot CHO$, melting at 105—106°, together with a *chloroditolyl*, $C_6H_4Me \cdot C_6H_4 \cdot CH_2Cl$, which melts at 109° after softening at 105°, and a little *dichloroditolyl*, $CH_2Cl \cdot C_6H_4 \cdot C_6H_4 \cdot CH_2Cl$, melting at 136—138°.

Dibenzyl yields benzaldehyde, some benzil and benzoin, deoxybenzoin, and benzophenone, together with α-stilbene dichloride and stilbene hydrochloride.   C. F. B.

2-Xylalphthalide. By Fritz Bethmann (*Ber.*, 1899, **32**, 1104—1113. Compare Heilmann, Abstr., 1891, 200, and A. Ruhemann, Abstr., 1892, 473, for 3- and 4-xylalphthalides).—*2-Xylalphthalide*, $CO{<}^{C_6H_4}_{\ \ O}{>}C{:}CH \cdot C_6H_4Me$, is obtained by heating phthalic anhydride (1 part) with 2-tolylacetic acid (1 part) and sodium acetate (0·02 part) for 10 hours at 240—250°, not more than 15—20 grams being used in one operation; it is yellow, and melts at 136·5°. When heated with aqueous caustic potash, it yields *α-2-methyldeoxybenzoin-2′-carboxylic acid*, $COOH \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot C_6H_4Me$; this melts at 131°, and forms a blue, insoluble *copper* salt, which melts at 179°, after softening at 160°. The *amide* of this acid is obtained when the phthalide is heated with alcoholic ammonia for 2 hours at 100°; it is yellowish-white, and melts at 155°; when boiled with acetic acid for 10 minutes, it yields *2-xylalphthalimidine*, $CO{<}^{C_6H_4}_{NH}{>}C{:}CH \cdot C_6H_4Me$, which is yellow, and melts at 196—197°.

α-2-Methyldeoxybenzoin-2′-carboxylic acid yields the *oximidolactone of phenyl-2-xylylketoxime-2′-carboxylic acid*, $CO{<}^{C_6H_4}_{O-N}{\geqslant}C \cdot CH_2 \cdot C_6H_4Me$, melting at 138·5° when it is dissolved in aqueous soda, the solution boiled with hydroxylamine, and then acidified with hydrochloric acid. When it is boiled with phenylhydrazine and acetic acid in alcoholic solution, it yields *phenyl-2-xylylphthalazone*,

$$CO{<}^{\overline{\quad C_6H_4 \quad}}_{CO \cdot NPh \cdot N}{>}C \cdot CH_2 \cdot C_6H_4Me,$$
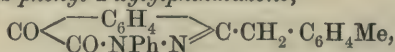
which melts at 177°; when it is reduced in cooled alkaline solution with $2\frac{1}{2}$ per cent. sodium amalgam, it yields the sodium salt of *α-2′-methyltoluylenehydrate-2-carboxylic* [*α-hydroxy-2′-methyldibenzyl-2-carboxylic*] *acid*, $COOH \cdot C_6H_4 \cdot CH(OH) \cdot CH_2 \cdot C_6H_4Me$; when this is decomposed with hydrochloric acid and the precipitate crystallised from alcohol, monoclinic crystals [$a:b:c = 1:?:0.7880$; $\beta = 113\frac{1}{2}°$] of *2-xylylphthalide*, $CO{<}^{C_6H_4}_{\ \ O}{>}CH \cdot CH_2 \cdot C_6H_4Me$, melting at 87°, are obtained. If the alkaline solution is not decomposed with hydrochloric acid, but concentrated on the water-bath, a syrup separates, and this, when heated for 5 hours at 200° and treated with dilute hydrochloric acid, yields *2′-methylstilbene-2-carboxylic acid*, $COOH \cdot C_6H_4 \cdot CH{:}CH \cdot C_6H_4Me$, which melts at 169°; its green, insoluble copper salt melts and decomposes at about 150°.

2′-Methylstilbene-2-carboxylic acid, when reduced with $2\frac{1}{2}$ per cent. sodium amalgam in alkaline solution, yields *2′-methyldibenzyl-2-carboxylic acid*, $COOH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot C_6H_4Me$, which melts at 123°. When treated with bromine in acetic acid solution, it yields *bromo-2-tolyldihydroisocoumarin*, $CO{<}^{C_6H_4 \cdot CHBr}_{\qquad O}{>}CH \cdot C_6H_4Me$, melting at 101—102°; if the product, instead of being precipitated with water, is boiled down and distilled under a pressure of 12 mm., the bromine is entirely removed; acetic acid distils over first, and then, at 220—240°, *2-tolylisocoumarin*, $CO{<}^{C_6H_4 \cdot CH}_{\qquad O}{>}C \cdot C_6H_4Me$,

which forms yellow, rhombic crystals $[a : b : c = 0\cdot7526 : 1 : 0\cdot5499]$ and melts at $102\cdot5°$.

2-Tolylisocoumarin, when treated with concentrated caustic potash solution, yields a syrup from which hydrochloric acid precipitates β-2'-*methyldeoxybenzoin-2-carboxylic acid*, $COOH\cdot C_6H_4\cdot CH_2\cdot CO\cdot C_6H_4Me$, melting at 139°. When this acid is reduced with sodium amalgam in alkaline solution, the product is β-*hydroxy-2'-methyldibenzyl-2-carboxylic acid*, $COOH\cdot C_6H_4\cdot CH_2\cdot CH(OH)\cdot C_6H_4Me$, which melts and decomposes at 137°. When the potassium salt of this acid is heated, 2'-methylstilbene-2-carboxylic acid (see above) is formed ; but when the free acid is heated to 150°, the product is 2-*tolyldihydroisocoumarin*,

$$CO{<}^{C_6H_4\cdot CH_2}_{\underline{}O}{>}CH\cdot C_6H_4Me,$$ which melts at 117°. When 2-tolyliso-

coumarin is heated with alcoholic ammonia for 12 hours at 100°, 2-*tolylisocarbostyril*, $CO{<}^{C_6H_4\cdot CH}_{\underline{}NH\underline{}}{>}C\cdot C_6H_4Me$, melting at 179°, is

formed, and when this is heated with phosphorus oxychloride for half an hour on the water-bath, the product is *chloro-2-tolylisoquinoline*,

$CCl{<}^{C_6H_4\cdot CH}_{N\underline{}}{>}C\cdot C_6H_4Me$, which melts at 67°, forms monoclinic

crystals $[a : b : c = 1\cdot3586 : 1 : 1\cdot05065 ; \ \beta = 119° \ 45']$, and yields 2-*tolylisoquinoline* when boiled for 3 hours with hydriodic acid (boiling at 127°) and red phosphorus. The last base melts at 78—79° ; its *hydrochloride*, *hydrobromide*, yellow *hydriodide*, *picrate*, *sulphate*, and orange *platinochloride* (with $2H_2O$) melt and decompose at about 221°, 235°, 190°, 150°, 212°, and 210° respectively. C. F. B.

Action of the Bis-diazochlorides of Benzidine, Orthotolidine, and Dianisidine on Ethylic and Methylic Malonates. By G. FAVREL (*Compt. rend.*, 1899, **128**, 829—830. Compare this vol., i, 438).—The action of these malonates on tetrazodiphenyl chloride yields *ethylic diphenyldihydrazonemalonate*, $C_{12}H_8[NH\cdot N\!:\!C(COOEt)_2]_2$, which forms yellow lamellæ melting at 178—180°, and the *methylic* salt which melts at 217—220°. Tetrazo-orthoditolyl chloride, under similar conditions, yields *ethylic ditolyldihydrazonemalonate* melting at 188—190°, and the *methylic* salt which melts at 210—212°, whilst the bis-diazochloride prepared from dianisidine yields *ethylic orthodianisyldihydrazonemalonate* which melts at 190—192°, and the *methylic* salt which melts at 268—270°. C. H. B.

Phenyldimethylcoumalin. By UGO BOSSI (*Gazzetta*, 1899, **29**, i, 1—12).—Ciamician and Silber (Abstr., 1894, i, 300) showed that, on treatment with alkalis, phenylcoumalin is resolved into acetophenone and formylacetic acid ; this transformation they regard as taking place in several stages, the lactone giving first a hydroxy-acid, then a ketonic acid, which, by taking up a mol. of water, is converted into acetophenone and formylacetic acid. They were not able, however, to isolate the intermediate ketonic acid, namely, γ-benzoylcrotonic acid.

In the case of the phenyldimethylcoumalin prepared by Ciamician and Silber (*loc. cit.*), the author finds that, on interaction with the calculated quantity of cold alcoholic potash, it gives as sole product

benzoyldimethylcrotonic acid, $COPh \cdot CHMe \cdot CMe \vdots CH \cdot COOH$. This acid separates in two forms; one, probably the fumaroid compound, crystallising from light petroleum in star-shaped groups of fine needles which melt at 101°, and are insoluble in water, slightly soluble in light petroleum, more so in aqueous alcohol, benzene, or ethylic acetate. The other, probably the maleoid form, is an oil having a characteristic odour, and is converted by concentrated hydrochloric acid into the fumaroid isomeride.

By the action of phenylhydrazine on benzoyldimethylcrotonic acid, no hydrazone is obtained, but 1 : 3-*diphenyl*-4 : 5-*dimethyl*-5-*pyrazoline-acetic acid*,

$$\begin{array}{c} CPh \cdot CHMe \\ \| \\ N \text{———} NPh \end{array} \!\!\! > CMe \cdot CH_2 \cdot COOH,$$

which crystallises in shining, yellow scales, melts at 169—170°, and is slightly soluble in light petroleum, more so in benzene and ethylic acetate. It forms an unstable silver salt, but its potassium, sodium, barium, calcium, and strontium salts are stable and crystallise from water in lustrous yellow laminæ.

Hydroxylamine resembles phenylhydrazine in its action on dimethylbenzoylcrotonic acid, giving 2-*phenyl*-3 : 4-*dimethyl*-4-*isoxazoleacetic acid*,

$$CPh \!\! < \!\! \begin{array}{c} CHMe \\ N \text{—} O \end{array} \!\! > \!\! CMe \cdot CH_2 \cdot COOH,$$

a yellow oil soluble in solutions of alkalis, alkali carbonates, and ammonia, and forming a stable silver salt.

On reduction with sodium amalgam, benzoyldimethylcrotonic acid gives a mixture of di- and tetra-hydrodimethylphenylcoumalins, and on treatment with ammonium acetate and acetic acid it yields 2-*phenyl*-3 : 4-*dimethyl*-6-*pyridone* (α-phenyl-α'-lutidone), which crystallises from benzene in colourless, transparent rhombohedra melting at 166°.   T. H. P.

Reactions of Indones and Quinones with Derivatives of Malonic Acid. By CARL LIEBERMANN (*Ber.*, 1899, **32**, 916—925. Compare this vol., i, 373).—Dihalogen derivatives of indones and quinones, as a rule, react only with 1 mol. of a derivative of malonic acid, but with ethylic cyanacetate in some cases both the halogen atoms are replaced. Dichlorindone reacts only with 1 mol. of this substance, yielding *ethylic chlorindonecyanacetate*,

$$CO \!\! < \!\! \begin{array}{c} CCl \\ C_6H_4 \end{array} \!\! > \!\! C \cdot CH(CN) \cdot COOEt,$$

which crystallises in colourless needles melting at 118°.

Dibromindone yields a mixture of *ethylic bromindonecyanacetate*, $C_{14}H_{10}BrNO_3$, melting at 134—135°, and *diethylic indonedicyanacetate*,

$$\begin{array}{c} CO \text{——} C \cdot CH(CN) \cdot COOEt \\ | \quad\quad \| \\ C_6H_4 \cdot C \cdot CH(CN) \cdot COOEt \end{array},$$

which forms yellow crystals melting at 142—143°. 2 : 3-Dichloro-α-naphthaquinone behaves in a similar manner, yielding *ethylic chloro-α-naphthaquinonecyanacetate*, $C_{15}H_{10}ClNO_4$, melting at 118°, and *diethylic α-naphthaquinonedicyanacetate*,

$$C_6H_4 \!\! < \!\! \begin{array}{c} CO \cdot C \cdot CH(CN) \cdot COOEt \\ CO \cdot C \cdot CH(CN) \cdot COOEt \end{array},$$

melting at 203—204°.

The halogen atom of the monohalogen product formed from a

dihalogen quinone and 1 mol. of a derivative of malonic acid can be readily replaced by substituted amido-groups. Ethylic bromo-a-naphthaquinonemalonate readily reacts with ethylamine, forming *ethylic ethylnaphthindolinonequinonecarboxylate*,

$$C_6H_4 < \begin{matrix} CO \cdot C \cdot NEt \\ CO \cdot C \cdot CH(COOEt) \end{matrix} > CO,$$

which is probably formed from the direct product of the action of ethylamine by the loss of the elements of alcohol. This substance crystallises in silky, yellow needles, which melt and decompose at 195°, and forms a blue solution in dilute alkalis and alkali carbonates. It is accompanied by a second compound containing bromine and nitrogen, which crystallises in red prisms and melts at 131°.

Paratolylnaphthindolinonequinonecarboxylic toluidide,

$$C_6H_4 < \begin{matrix} CO \cdot C \cdot N \cdot C_7H_7 \\ CO \cdot C \cdot CH(CO \cdot NH \cdot C_7H_7) \end{matrix} > CO,$$
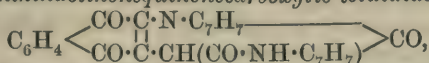
is prepared by boiling ethylic bromonaphthaquinonemalonate with alcoholic toluidine, and crystallises in red needles melting at 285°. When the boiling is only continued for a short time, on the other hand, the product consists of the *paratoluidide* of *diethylic a-naphthaquinonemalonate*, $C_6H_4 < \begin{matrix} CO \cdot C \cdot NH \cdot C_7H_7 \\ CO \cdot C \cdot CH(COOEt)_2 \end{matrix}$, which crystallises in red needles melting at 122—124°.

Bischlorindonephloroglucinol is converted by acetic anhydride and sodium acetate into a *triacetyl* derivative, $C_6H(OAc)_3 \Big(C \lll \begin{matrix} CO \\ CCl \end{matrix} > C_6H_4 \Big)_2$, melting at 203°. This shows that, in its reaction with dichlorindone, phloroglucinol has behaved as a hydroxyl derivative, and not as a ketone.

Chlorindoneresorcinol ether, $C_6H_4 < \begin{matrix} CO \\ CCl \end{matrix} > C \cdot O \cdot C_6H_4 \cdot OH$, obtained by the action of resorcinol on dichlorindone in the presence of sodium ethoxide in the cold, crystallises in yellow needles melting at 163—164°, and forms an *acetyl* derivative melting at 97—98°. In boiling alcoholic solution, however, resorcinol yields *anhydroindoneresorcinol ether*, $\begin{matrix} CO—C \cdot O \\ C_6H_4 \cdot C \cdot C_6H_3 \cdot OH \end{matrix}$, which crystallises in red needles, decomposes when heated, and forms a blue solution in cold aqueous sodium carbonate; its *acetyl* derivative forms light-red, matted needles melting at 191—192°.

Anhydro-a-naphthaquinoneresorcinol, $C_6H_4 < \begin{matrix} CO \cdot C \cdot C_6H_3 \cdot OH \\ CO \cdot C \cdot O \end{matrix}$, crystallises in reddish needles melting above 300°, and yields an *acetyl* derivative melting at 289°.

Ethylic glutaconate reacts in a similar manner to ethylic malonate with indones and quinones, but the colour reactions of the products are somewhat different. **A. H.**

3 : 2′-Dihydroxyflavone. By STANISLAUS VON KOSTANECKI and R. VON SALIS (*Ber.*, 1899, **32**, 1030—1034).—By combining ethylsalicylic aldehyde with the monethylic ether of resacetophenone, under the same conditions as were observed in the case of monethylic

ether of benzylideneresacetophenone, the *ethylic ether* of 2-*ethoxy-benzylideneresacetophenone*, $OEt \cdot C_6H_3(OH) \cdot CO \cdot CH \colon CH \cdot C_6H_4 \cdot OEt$ [= 4 : 2 : 2'], is formed; it crystallises from alcohol in reddish-yellow prisms melting at 125°. The *acetyl* derivative crystallises from alcohol in light yellow plates melting at 78—90°, and on treatment with bromine in carbon bisulphide solution takes up 2 atoms of bromine without evolution of hydrogen bromide, forming a thick syrup, which probably consists of the *dibromide*, since on treatment with alcoholic potassium hydroxide it yields 3 : 2'-*diethoxyflavone*,

$$OEt \cdot C_6H_3 {\displaystyle \mathop{<}^{O-\underset{\|}{C} \cdot C_6H_4 \cdot OEt}_{CO \cdot CH}} \quad [OEt = 3 : 2'] \, ;$$
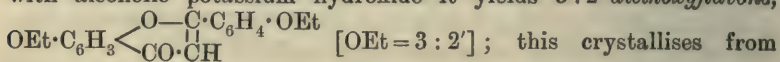
this crystallises from alcohol in prisms melting at 125°, and is coloured yellow by concentrated sulphuric acid, the solution gradually losing its colour and assuming a bright blue fluorescence.

On treatment with sodium ethoxide, 3 : 2'-diethoxyflavone is entirely resolved into the monethylic ether of resacetophenone and salicylic acid, and on treatment with hydriodic acid is converted into 3 : 2'-*dihydroxyflavone*, a substance which crystallises in microscopic needles melting at 320°; with sulphuric acid, it behaves in the same way as the diethylic ether, and dissolves in sodium hydroxide solution with a yellow coloration. 3 : 2'-*Diacetoxyflavone* crystallises from dilute alcohol in white crystals melting at 105°.   J. F. T.

4'-Hydroxy-α-naphthaflavone. By E. KELLER and STANISLAUS VON KOSTANECKI (*Ber.*, 1899, **32**, 1034—1037).—Emilewicz and Kostanecki's method (Abstr., 1898, i, 369) for the preparation of flavones applies also in the naphthalene series, since on condensing 2-acetyl-1-naphthol with anisaldehyde in the usual way, 2-*anisylideneacetyl-1-naphthol*, $OH \cdot C_{10}H_6 \cdot CO \cdot CH \colon CH \cdot C_6H_4 \cdot OMe$, is formed as an orange-coloured substance crystallising from benzene or glacial acetic acid in needles melting at 158°. Its *acetyl* derivative crystallises in light yellow needles melting at 96°, and on bromination passes into the *dibromide* which separates from a mixture of chloroform and ether in white needles melting at 135·5°; this dibromide is converted by alcoholic potassium hydroxide into 4'-*methoxy-α-naphthaflavone*,

$$C_{10}H_6{\overset{(\alpha)}{\underset{(\beta)}{}}} {\displaystyle \mathop{<}^{O-\underset{\|}{C} \cdot C_6H_4 \cdot OMe}_{CO \cdot CH}} \, ,$$
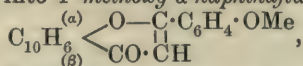
which crystallises in light yellow needles melting at 181°; its solution in strong sulphuric acid is yellow, with a green fluorescence.

4'-Methoxy-α-naphthaflavone is resolved by sodium ethoxide into 2-acetyl-1-naphthol and anisic acid, and on boiling for many hours with hydriodic acid gives the corresponding 4'-*hydroxy-α-naphthaflavone*, a colourless substance crystallising in needles melting at 315—316°; it dissolves in sodium hydroxide solution with a yellow colour, and behaves towards sulphuric acid in the same way as the methylic ether. 4'-*Acetoxy-α-naphthaflavone* crystallises from glacial acetic acid and alcohol in white needles melting at 215°.   J. F. T.

2'-Ethoxy-α-Naphthaflavone. By D. ALPERIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1899, **32**, 1037—1039. Compare preceding abstract).—*Orthethoxy-2-benzylideneacetyl-1-naphthol* crystallises from

glacial acetic acid in orange-red needles melting at 154—155°, which are coloured red by concentrated sulphuric acid; the *acetyl* derivative crystallises in light orange leaflets melting at 125—126°, and the *dibromide* in colourless prisms melting at 155—156°. 2′-*Ethoxy-α-naphthaflavone* separates from alcohol in pale yellow needles melting at 160°, and dissolves in concentrated sulphuric acid to a light orange solution showing an intense green fluorescence; it is decomposed by sodium ethoxide into acetylnaphthol and salicylic acid.

Furfuraldehyde combines with 2-acetyl-1-naphthol, forming 2-*furfurylideneaceto-1-naphthol*, $OH \cdot C_{10}H_6 \cdot CO \cdot CH \colon CH \cdot C_4H_3$, which crystallises in red needles or leaflets melting at 121—122°; the *acetyl* derivative separates from alcohol in yellow plates melting at 116—117°, but on bromination does not yield the desired dibromide.   J. F. T.

The Seventh Isomeride of Rosinduline. By FRIEDRICH KEHRMANN and M. RAVINSON (*Ber.*, 1899, **32**, 927—932. Compare Abstr., 1898, i, 155; and this vol., i, 235 and 238).—2″-*Acetamido-phenylisonaphthaphenazonium chloride*, $NHAc \cdot C_{10}H_5 \underset{N}{\overset{NPhCl}{\lessgtr}} C_6H_4$,

is formed when orthamidodiphenylamine hydrochloride dissolved in the smallest possible quantity of alcohol to which a few drops of hydrochloric acid have been added, is mixed with 3′-acetamido-1 : 2-naphthaquinone suspended in alcohol and the mixture warmed on the water-bath to the boiling point of the alcohol; when purified by solution in water and precipitation with hydrochloric acid, it forms orange-yellow, crystalline nodules with a green, metallic lustre; its alcoholic solution exhibits an orange-red colour with a distinct yellow fluorescence. The *platinochloride*, $(C_{24}H_{17}N_3O)_2,H_2PtCl_6$, forms a brick-red, crystalline powder, and the *dichromate*, $(C_{24}H_{18}N_3O)_2Cr_2O_7$, crystallises in small, brownish-red plates.

2″-*Amidophenylisonaphthaphenazonium chloride*, $C_{22}H_{16}N_3Cl$, obtained when the acetyl derivative is warmed with dilute hydrochloric acid until the solution assumes a pure violet colour, is precipitated by the addition of solid sodium chloride and purified by crystallisation from very dilute hydrochloric acid, and thus forms dark violet, laminated plates with a coppery lustre. Its aqueous and alcoholic solutions are pure violet in colour and exhibit no fluorescence; its *platinochloride* forms a violet-coloured, lustrous precipitate. The above chloride is the seventh isomeride of rosinduline which has been prepared; its constitution as a phenylisonaphthaphenazonium derivative follows from the fact that, when the amido-group is eliminated, phenylisonaphthaphenazonium is obtained.

Isorosinduline No. 7 does not react with amines, but its acetyl derivative forms condensation products with aniline or ammonia, the hydrogen in the para-position (3) to the azine nitrogen atom becoming replaced by NH_2 and $NHPh$ respectively.

3-*Anilido-2″-acetamidophenylisonaphthaphenazonium chloride*,

$$NHAc \cdot C_{10}H_5 \underset{N}{\overset{NPhCl}{\lessgtr}} C_6H_3 \cdot NHPh,$$
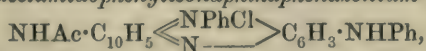
is readily formed when an alcoholic solution of the chloride of the acetyl derivative is allowed to remain in contact with an excess of

aniline and the theoretical amount of aqueous sodium hydroxide for 24 hours and the product then acidified with hydrochloric acid ; after recrystallisation from boiling alcohol, it forms a microcrystalline powder with a coppery lustre, is only sparingly soluble in water, somewhat more readily in hot alcohol or acetic acid, yielding bluish-black solutions.

The *hydroxide*, $C_{30}H_{24}N_4O_2$, is obtained in the form of a black, crystalline powder when an alcoholic solution of the chloride is treated with water and a slight excess of sodium carbonate. When the chloride is hydrolysed with hydrochloric acid and alcohol, *3-anilido-2''-amidophenylisonaphthaphenazonium chloride* is obtained in the form of needles having a coppery lustre ; it dissolves in water or alcohol, yielding blue solutions, and its *platinochloride*, $(C_{28}H_{20}N_4)_2,H_2PtCl_6$, forms a blue, crystalline powder.

3-Amido-2''-acetamidophenylisonaphthaphenazonium chloride, obtained by the action of an excess of ammonia on the chloride of acetyl-rosinduline No. 7, crystallises from alcohol in dark-red crystals with a brassy lustre ; its aqueous and alcoholic solutions have a dark blood-red colour and a fiery red fluorescence. When hydrolysed with hydrochloric acid, it yields *3 : 2''-diamidophenylisonaphthaphenazonium chloride* in the form of metallic green crystals, which dissolve in water or alcohol with a pure violet, and in concentrated sulphuric acid with a reddish-brown, colour. The *platinochloride*, $(C_{22}H_{16}N_4)_2,H_2PtCl_6$, forms a dark violet, crystalline powder practically insoluble in water.

<div align="right">J. J. S.</div>

Action of Amines on Salts of 3'-Acetamidophenylisonaph-thaphenazonium. By FRIEDRICH KEHRMANN and WALTHER AEBI (*Ber.*, 1899, **32**, 932—938).—Amines readily react with salts of 3'-acetamidophenylisonaphthaphenazonium (Abstr., 1896, i, 509), yielding substituted derivatives of the type

$$NHAc \cdot C_{10}H_5 \underset{N}{\overset{NPhCl}{\lessgtr}} C_6H_3 \cdot NHR,$$
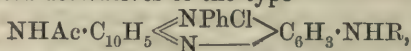
in which the amido- or substituted amido-group occupies the position 2 ; when these are hydrolysed, the corresponding 2 : 3'-diamido-derivatives are obtained, which are characterised by the readiness with which the amido-group in the position 3' can be replaced.

2-Amido-3'-acetamidophenylisonaphthaphenazonium chloride,

$$C_{24}H_{19}N_4OCl + H_2O,$$
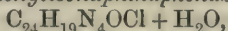
obtained by alternately saturating an alcoholic solution of the 3'-acet-amido-compound with ammonia and then removing the excess of ammonia by a current of air, is precipitated by the addition of dilute hydrochloric acid to its aqueous solution in the form of reddish-violet needles with a metallic lustre ; its alcoholic solution has a red fluores-cence, and that in concentrated sulphuric acid a dirty violet colour. The *nitrate* forms reddish-violet needles sparingly soluble in water, and the *platinochloride* brownish-red needles practically insoluble in water.

2 : 3'-Diamidophenylisonaphthaphenazonium chloride, $C_{22}H_{17}N_4Cl + H_2O$, obtained by carefully hydrolysing the acetamido-derivative with sul-phuric acid and water, precipitating with sodium chloride, and crys-tallising from water containing a little hydrochloric acid, forms

greenish-blue needles with a steely lustre, and is readily soluble in alcohol and hot water; its *platinochloride* is a black, crystalline powder practically insoluble in water. It is impossible to avoid the formation of 2-*amido*-3′-*hydroxyphenylisonaphthaphenazonium* during the hydrolysis; this is, however, precipitated as its *sulphate* in the form of dark blue needles, and dissolves fairly readily in water to a bluish-violet solution. The sulphate is most readily obtained by boiling the diamine with dilute sulphuric acid for half an hour; ammonia decomposes it into an anhydride of the base, namely, 2-*amidonaphtha-prasindone*, $O{<}\genfrac{}{}{0pt}{}{NPh=C_6H_3\cdot NH_2}{C_{10}H_5\cdot N}$, which forms bluish-green needles soluble in boiling water or concentrated sulphuric acid.

2-*Dimethylamido*-3′-*acetamidophenylisonaphthaphenazonium chloride*, $C_{26}H_{23}N_4OCl$, after purification by repeated solution in water, filtration, and precipitation with hydrochloric acid, forms blue needles which contain $1H_2O$, even when dried at 150°; the *nitrate*, $C_{26}H_{23}N_4O\cdot NO_3 + H_2O$, crystallises in glistening, blue needles sparingly soluble in water; the *platinochloride* forms slender, blue needles insoluble in water, and the *aurichloride* a dark blue, flocculent precipitate.

2-*Dimethylamidonaphthaprasindone sulphate* crystallises from its hot aqueous sulphuric acid solution in dark greenish-blue needles with a coppery lustre; when boiled with water, it undergoes dissociation, and the *prasindone* is precipitated; this is more readily obtained by the action of ammonia on the sulphate, and forms light, pale green needles insoluble in water.

2-*Anilido*-3′-*acetamidophenylisonapthaphenazonium chloride*,

$$NHAc\cdot C_{10}H_5{\ll}\genfrac{}{}{0pt}{}{NPhCl}{N\underline{\quad\quad}}{>}C_6H_3\cdot NHPh,$$
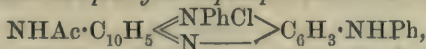
crystallises in coppery plates practically insoluble in cold water, but dissolving in alcohol to a dark blue solution; when treated with sodium carbonate, it yields an *anhydride*, $C_{30}H_{22}N_4O$, in the form of slender, dark blue needles; this anhydride must have either a prasindone or rosindone constitution. The *nitrate*, $C_{30}H_{23}N_4O\cdot NO_3$, forms slender, blue needles insoluble in water; the *platinochloride*, $(C_{30}H_{22}N_4O)_2,H_2PtCl_6$, in microscopic crystals, and the *aurichloride*, $C_{30}H_{22}N_4O,HAuCl_4$, have been prepared. J. J. S.

Naphthindulines and Naphthazonium Compounds. By FRIEDRICH KEHRMANN and W. F. SUTHERST (*Ber.*, 1899, **32**, 939—947). —An acetic acid solution of 4-acetamido-1 : 2-naphthaquinone (Abstr., 1895, i, 151) readily condenses with phenylorthonaphthylenediamine hydrochloride (Abstr., 1887, 590), yielding a mixture of two isomeric chlorides, $C_{28}H_{20}N_3OCl$. The one, 4-*acetamidophenyldinaphthazonium chloride*, $NHAc\cdot C_{10}\overset{1,2}{H_5}{\ll}\genfrac{}{}{0pt}{}{N\underline{\quad\quad}}{NPhCl}{>}\overset{1,2}{C_{10}}H_6$, is sparingly soluble in acetic acid and the greater part crystallises out after the mixture has been kept for 4 days at the ordinary temperature; it may be purified by crystallisation from boiling alcohol, and is thus obtained in the form of brick-red needles with a green, metallic lustre; its solutions, especially

in dilute alcohol, exhibit a strong, orange-yellow fluorescence. The *nitrate*, $C_{28}H_{20}N_3O \cdot NO_3$, forms brick-red needles sparingly soluble in water; the *platinochloride*, glistening, golden-red plates, and the *dichromate*, an insoluble crystalline precipitate. When an alcoholic solution of the sparingly soluble chloride is boiled with dilute sulphuric acid, the greater part of the alcohol distilled off, and sodium chloride added, *amidophenyldinaphthazonium chloride* is obtained; this crystallises from alcohol in dark-red, glistening needles sparingly soluble in water, alcohol, or acetic acid. The *nitrate* is also sparingly soluble in water and crystallises in metallic green needles. These salts are identical with those obtained from Fischer and Hepp's so-called naphthinduline (Abstr., 1893, i, 333). The base melts at 253—255° (according to Fischer and Hepp, at 248—250°). It is undoubtedly an azonium compound, and is to be regarded as the "rosinduline" of di-naphthazonium, since, when the amido-group is eliminated, salts of phenyldinaphthazonium are obtained. *Phenyldinaphthazonium chloride,*

$$C_{10}H_6 \ll^{N}_{NPhCl} > C_{10}H_6,$$

crystallises from alcohol in reddish-brown, glistening needles, and is sparingly soluble in water, the solution exhibiting a strong, yellowish-green fluorescence. The *nitrate* is precipitated from an aqueous solution of the chloride by dilute nitric acid; the *platinochloride* crystallises in golden-brown, glistening plates.

The more soluble of the two isomeric chlorides, 4-*acetamidophenyl-isodinaphthazonium chloride,* $NHAc \cdot \overset{4}{C_{10}}\overset{1,2}{H_5} \ll^{NPhCl}_{N} > \overset{3,4}{C_{10}}H_6,$ crystallises from alcohol in brick-red, felted needles, and is fairly readily soluble in water or acetic acid, yielding dark-red solutions which are not fluorescent; the *nitrate* forms dark-red needles practically insoluble in water, and the *dichromate* a violet-red powder. *Amidophenylisodi-naphthazonium chloride*, obtained by hydrolysing the acetamido-compound with sulphuric acid and precipitating with sodium chloride, crystallises from alcohol in green needles soluble in alcohol to a bluish-green and in water to a violet-blue solution. The *nitrate* crystallises in bluish-green needles very sparingly soluble in water.

4-*Hydroxyphenylisodinaphthazonium chloride,*

$$OH \cdot C_{10}H_5 \ll^{NPhCl}_{N} > C_{10}H_6,$$
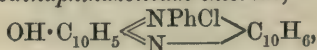
obtained by boiling the amido- or acetamido-derivative with an excess of sulphuric acid, dissolving the hydroxy-sulphate thus formed in water, and precipitating with hydrochloric acid, forms chocolate-coloured needles; the *nitrate* crystallises in violet-brown needles. The *base* appears to exist only in the form of an anhydride, *dinaphthaprasindone,*

$$O \ll^{NPh=C_{10}H_6}_{C_{10}H_5 \cdot N},$$
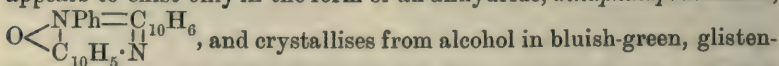
and crystallises from alcohol in bluish-green, glistening plates; when treated with acetic anhydride, it forms an *acetyl* derivative, which yields a *nitrate*, $OAc \cdot C_{10}H_5 \ll^{NPh(NO_3)}_{N} > C_{10}H_6,$ crystallising from alcohol or ether in brassy, brown-red plates readily soluble in water or alcohol, and a *platinochloride*, forming golden-red, glistening plates insoluble in water.   J. J. S.

Action of some Copper Salts on β-Naphthol. By R. Fosse (*Bull. Soc. Chim.*, 1898, [iii], 19, 610—611).—β-Naphthol is oxidised by cupric acetate, formate, chloride, or nitrate in boiling aqueous solution with the formation of $\beta\beta$-dinaphthol. The addition of a little ammonia favours oxidation by neutralising the acid liberated in the reaction. Cupric sulphate and potassium cupric tartrate are without action on β-naphthol. α-Naphthol is distinguished from β-naphthol by yielding, under the same conditions, a deep violet precipitate which could not be obtained in a crystalline form. N. L.

Action of Ethylenic Bromide on $\beta\beta$-Dinaphthol. By R. Fosse (*Bull. Soc. Chim.*, 1898, [iii], 19, 611—612).—When $\beta\beta$-dinaphthol is heated at 150° with alcoholic potash and ethylenic bromide, *dinaphthyl ethylenic ether*, $C_{20}H_{12}\!\!<^{O\cdot CH_2}_{O\cdot CH_2}$, is formed; it is crystalline and melts at 196—197°. N. L.

Action of Methylenic Chloride on $\beta\beta$-Dinaphthol. By R. Fosse (*Bull. Soc. Chim.*, 1898, [iii], 19, 612).—When a mixture of $\beta\beta$-dinaphthol with methylenic chloride and alcoholic potash is heated in a sealed tube, *dinaphthyl methylenic ether*, $C_{20}H_{12}\!\!<^{O}_{O}\!\!>CH_2$, is obtained; it does not crystallise well.

The *diacetate* of $\beta\beta$-dinaphthol, $C_{20}H_{12}(OAc)_2$, melts at 109°, is soluble in alcohol and ether, insoluble in alkalis, and gives a rose coloration with sulphuric acid. N. L.

Constitution of Terpenes and Allied Compounds. By K. Slawinski (*Chem. Centr.*, 1898, ii, 543—544; from *J. Russ. Chem. Soc.*, 1898, 30, 195—214).—The pinolglycol prepared from dibromopinol and that obtained by oxidising pinol with potassium permanganate are stereoisomerides. The latter boils at 281—282°, is easily soluble in water, alcohol, ether, or glacial acetic acid, and slightly in light petroleum; it crystallises from water in monoclinic plates melting at 128—129°, from ethylic acetate in rhombic prisms melting at 126—127°, and when sublimed forms thin leaflets which melt at 128·5—129·5°. The acetyl derivative, $C_{10}H_{16}O(OAc)_2$, prepared by heating with acetic anhydride, is a thick, optically inactive syrup, slightly soluble in water, boils at 165—167° under 17 mm. pressure, and has a sp. gr. 1·1360 at 20°/20°; when hydrolysed, it yields the original glycol melting at 128—129°, and when heated with phenylcarbimide forms a mixture of mono- and di-urethanes which melts at 151—154°. The acetyl derivative, $C_{10}H_{16}O(OAc)_2$, obtained from silver acetate, glacial acetic acid, and dibromopinol, melts at 97°, boils at 151—152° under 8·5 mm. pressure, and yields Wallach's pinene glycol, which melts at 123—124° and boils at 158—159° under 12 mm. pressure. Wallach's acetyl derivative melts at 97° and boils at 151—152° under 85 mm. pressure, whilst Wagner's pinolglycol from pinol melts at 128·5—129°, boils at 157—158° under 12 mm. pressure, and yields a liquid acetyl derivative which boils at 154—155° under 10·5 mm. pressure. The glycols prepared from the acetyl derivatives, when oxidised with a 5 per cent. solution of potassium permanganate (4 mols. oxygen to 1

mol. glycol), yield acetic and terpenylic acids, and in one experiment the liquid glycol gave a little terebic acid. The reactions of the glycols indicate the same structural formula, and the method of formation of sobrerol from pinol by means of the additive bromine compound, $C_{10}H_{16}(OH)_2Br_2$, shows that the OH-groups are in the *cis*-position and hence the oxides, when hydrogenised, form the *cis*-glycol identical with that from dibromopinol. The author combats Ginzberg's views (*J. Russ. Chem. Soc.*, **29**, 267), and considers his formula for sobreritol unsatisfactory. Pinene glycol is a partial anhydride of the tetrahydric sobreritol, and hence may be considered as a dihydric alcohol of the a- and an oxide of the γ-series. This combination of a secondary and tertiary alcohol with an oxide confers characteristic properties on the glycol and its derivatives : thus dibromopinol loses its bromine even by the action of silver nitrate in alcoholic solution, but does not readily yield hydrogen bromide ; the acetyl derivatives also are extremely easily hydrolysed. The glycol does not lose water at 150°, but by the action of 2 per cent. hydrochloric acid solution, water is removed and an unsaturated compound formed. The similarity of the reactions of the polymethylene compounds and the aliphatic glycols is pointed out, thus trimethylethylenic glycol, by the action of acetic anhydride, yields unsaturated compounds and the acetyl derivative, $C_5H_{10}(OAc)_2$.

E. W. W.

Action of Formaldehyde on Menthol and Borneol. By ANDRÉ BROCHET (*Compt. rend.*, 1899, **128**, 612—613. Compare this vol., i, 376).—The *methylenic acetal* of *menthol* (*dimentholic formal*),

$$CH_2(O \cdot C_{10}H_{19})_2,$$
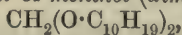
obtained by the condensation of menthol with formaldehyde in the presence of mineral acids, crystallises from alcohol in colourless, silky needles, melts at 56·5°, and boils with slight decomposition at 337° under ordinary pressure. It has a disagreeable odour, unlike that of menthol, and may be distilled without alteration under reduced pressures.

The *methylenic acetal* of *borneol* (*diborneolic formal*), $CH_2(O \cdot C_{10}H_{17})_2$, crystallises from alcohol in nacreous lamellæ, melts at 166°, and distils unchanged at 344—345° under ordinary pressure. It is very soluble in the ordinary organic solvents, and has an odour resembling that of borneol, which is not removed by repeated crystallisation and distillation. These substances are not hydrolysed by water or a 15 per cent. solution of sodium hydroxide even at 150°.

The corresponding derivatives of linalool and geraniol could not be obtained owing to the action of the mineral acid on these alcohols.

G. T. M.

Terpenes and Ethereal Oils. The Carvone Series. By OTTO WALLACH (*Annalen*, 1899, **305**, 223—259).—[With H. LÖHR and E. LIPCZYNSKI.]—The compound, $C_{20}H_{30}O_2$, produced along with dihydrocarvone when carvone is reduced with alcohol and sodium (Wallach and Schrader, Abstr., 1894, i, 537), is not a pinacone, but a ketone, *dicarvelone*. It has been obtained in nine forms, of which the a-modifications are obtained from carvone by the action of alcoholic potash and zinc dust, and give rise to the β-isomerides when the hydrobromides are treated with alcoholic potash ; the γ-modifications

are obtained when the other forms are dissolved in concentrated sulphuric acid.

a-Dl-*Dicarvelone* melts at 148—149°, and has the specific rotatory power $[a]_D = -73\cdot9°$. *a*-Ld-*Dicarvelone* has $[a]_D = +73\cdot2°$. *a*-i-*Dicarvelone*, prepared by mixing equal weights of the foregoing modifications, also crystallises in the rhombic system and melts at 120—121°; the *phenylhydrazone* decomposes at about 200°, whilst the corresponding derivative of the active ketones melts at 215°. The active *dioxime* melts at 223°, and yields a *diacetyl* derivative melting at 187°; the derivatives of the racemic ketone melt at 287° and 166° respectively. The *dihydrobromide* of *a*-Dl-dicarvelone separates from alcohol in white crystals and melts at 165°.

β-Dd-*Dicarvelone*, prepared from *a*-Dl-dicarvelone, melts at 207°, and has the specific rotatory power $[a]_D = +79\cdot1°$. *β*-Ll-*Dicarvelone*, obtained from *a*-Ld-dicarvelone, has $[a]_D = -82\cdot6°$. *β*-i-*Dicarvelone* melts at 168°.

γ-Dl-*Dicarvelone*, derived from *a*-Dl-dicarvelone, melts at 126°, and has the specific rotatory power $[a]_D = -213\cdot4°$; *γ*-Dl-dicarvelone, prepared from *β*-Dd-dicarvelone, has $[a]_D = -201\cdot8°$. *γ*-Ld-*Dicarvelone* has $[a]_D = +236\cdot8°$. *γ*-i-*Dicarvelone* melts at 112°.

The constitution of *a*-dicarvelone and *β*-dicarvelone are represented by the formulæ

$$CH_2 {<}^{CO\text{————}CHMe}_{CH(CMe\vdots CH_2)\cdot CH_2}{>}CH\cdot CH{<}^{CHMe\text{————}CO}_{CH_2\cdot CH(CMe\vdots CH_2)}{>}CH_2$$

and

$$CH_2 {<}^{CO\text{——}CHMe}_{C(\vdots CMe_2)\cdot CH_2}{>}CH\cdot CH{<}^{CHMe\text{——}CO}_{CH_2\cdot C(\vdots CMe_2)}{>}CH_2$$
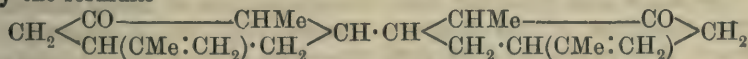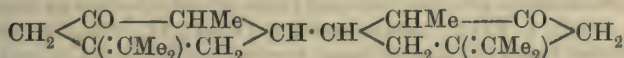
respectively.

Dieucarvelone, $C_{20}H_{30}O_2$, obtained by reducing eucarvone, carvone hydrochloride, or carvone ·hydrobromide with alcoholic potash and zinc dust, occurs in two modifications, which melt at 172° and 128° respectively.

[With H. Löhr.]—Eucarvone (von Baeyer, Abstr., 1894, i, 298) boils at 104—106° under 20 mm. pressure, and has a sp. gr. 0·952 at 20°, and a refractive index n_D 1·5048, whence $M = 46·72$.

Dihydroeucarvylamine, $C_{10}H_{17}\cdot NH_2$, prepared by reducing the oxime in alcoholic solution with sodium, boils at 116—117° under a pressure of 40 mm. (von Baeyer, Abstr., 1895, i, 152); the *phenylcarbamide*, $NHPh\cdot CO\cdot NH\cdot C_{10}H_{17}$, melts at 142°, and the *phenylthiocarbamide* crystallises from methylic alcohol in transparent plates and melts at 120—121°.

The compound, $C_{24}H_{24}O_2$, melting at 193—194°, is produced along with benzylidene-eucarvone when the ketone is condensed with benzaldehyde (Abstr., 1896, i, 573); its constitution is probably represented by the formula $C_7H_{10}{<}^{CH\cdot CHPh}_{CH\cdot CHPh}{>}CO{>}O$ (compare Vorländer, Abstr., 1898, i, 27).

[With C. Ohligmacher.]—The base, $C_{10}H_{15}NO$, obtained by the action of ammonia on racemic carvone tribromide (Abstr., 1895,

i, 622), yields an *oxime*, OH·$C_{10}H_{13}$:NOH, which crystallises from water in needles and melts at 100°; when the hydrochloride of the base is submitted to dry distillation, the *compound* $C_{10}H_{15}NO$ is formed, which melts at 165—167°.

Di-*Carvenolide*, $C_{10}H_{14}O_2$, is the lactone corresponding with the base derived from *d*-carvone, and melts at 41—42° (compare Abstr., 1895, i, 622); it has the specific rotatory power $[a]_D = -138.5°$, and the *dibromide*, which melts at 97—99°, has $[a]_D = -67.0°$. Ld-*Carvenolide* has $[a]_D = +143.3$. i-*Carvenolide* melts at 71—72°; the *dibromide* melts at 95—96°.

Dd-*Carvenolic acid*, $C_{10}H_{16}O_3$, obtained by the action of alcoholic sodium methoxide on the lactone from *d*-carvone, melts at 133°, and has the specific rotatory power $[a]_D = +178.7°$. i-*Carvenolic acid* melts at 135—136°.

The *acid*, $C_7H_{10}O_2$, produced on heating carvenolic acid with potash at 230—250°, melts at 130—131°, and is volatile in steam. The *dibromide*, $C_7H_{10}Br_2O_2$, melts and decomposes at 150°. Chromic and nitric acids oxidise carvenolic acid, forming the *acid* $C_7H_{10}O_4$, which melts at 201—202°.

Constitutional formulæ representing the foregoing substances are suggested.   M. O. F.

Terpenes and Ethereal Oils. Condensation of Benzaldehyde with Ketones of the Terpene Series. By OTTO WALLACH [and MILO C. BURT] (*Annalen*, 1899, **305**, 261—276).—Benzylidenementhone is the condensation product obtained from benzaldehyde and menthone (Abstr., 1896, i, 573). *Benzylmenthol*, OH·$C_{10}H_{18}$·CH_2Ph, obtained by reducing benzylidenementhone, crystallises from ether, and melts at 111—112°; it boils at 181—183° under 10 mm. pressure. *Methylisopropylhexahydrofluorene*, $\begin{matrix} CH_2 \cdot CHMe \cdot CH \cdot CH_2 \\ | \qquad\qquad | \quad | \\ CH_2 \cdot CHPr^\beta \cdot CH \cdot C_6H_4 \end{matrix}$, produced by the action of phosphoric anhydride on benzylmenthol, is a colourless liquid which boils at 153—155° under 10 mm. pressure; it does not decolorise a cold solution of potassium permanganate. *Benzylidenementhylamine*, $C_{17}H_{25}N$, formed on reducing benzylidenementhone-oxime in alcoholic solution with sodium, boils at 200—205° under 10 mm. pressure.

When dried hydrogen chloride is passed into a mixture of benzaldehyde and tetrahydrocarvone, the *compound* $C_{24}H_{28}O_2$ is produced; it crystallises from ethylic acetate and melts at 175°.

Benzylpulegol, OH·$C_{10}H_{16}$·CH_2Ph, obtained by reducing benzylidene-pulegone, is a viscous oil which boils at 192—195° under 10 mm. pressure; the *hydrocarbon*, $C_{17}H_{22}$, formed by the action of phosphoric anhydride, boils at 162—164° under 10 mm. pressure.

Benzylidenedihydrocarvone, $C_{10}H_{14}O$:CHPh, boils at 187—190° under 10 mm. pressure; the *oxime* crystallises from methylic alcohol in colourless needles and melts at 145—146°. *Benzyldihydrocarvol*, OH·$C_{10}H_{16}$·CH_2Ph, boils at 182—183° under 10 mm. pressure; the *hydrocarbon*, $C_{17}H_{22}$, obtained by the action of phosphoric anhydride, boils at 166—169° under 10 mm. pressure.

Carvenone resembles tetrahydrocarvone in its behaviour towards

benzaldehyde, yielding the *compound* $C_{24}H_{26}O_2$, in which the ketone is combined with 2 molecular proportions of the aldehyde; it crystallises from methylic alcohol, and melts at 170—171°. Menthenone gives rise to the *compound* $C_{24}H_{24}O$, which crystallises from alcohol in slender, pale yellow needles melting at 129—130°; reduction with zinc dust and acetic acid transforms it into the *compound* $C_{24}H_{26}O$, which melts at 72—75°.

A table comparing the physical properties of isomeric ketones, $C_{10}H_{16}O$, belonging to the terpene series is included in the paper.

M. O. F.

Essential Oil of Caparrapi. By F. J. TAPIA (*Bull. Soc. Chim.,* 1898, [iii], **19**, 638—644).—Oil of caparrapi is a thick liquid, of acid reaction and sweet, agreeable odour, which exudes from incisions made in the capelo tree (*Nectandra caparrapi*) of Colombia. It varies in colour from pale yellow to dark brownish-red, and two varieties are recognised in commerce, the "white" oil and the "black." The former has a sp. gr. 0·9336 at 15° and a rotatory power – 3°; when cooled to – 27°, it becomes turbid and semi-solid, and some specimens, when kept, deposit crystals of the acid described below. The black oil has a sp. gr. 0·9163 at 15°, is less viscid than the white, and remains fluid and transparent when cooled; both varieties are readily soluble in most organic solvents. From the white oil, by treatment with dilute aqueous soda or lime-water and subsequent acidification with hydrochloric acid, an *acid*, $C_{15}H_{26}O_3$, is obtained which crystallises in white needles, melts at 84·5°, has a rotatory power $[a]_D = +3°$ in alcoholic solution, and is very slightly soluble in cold, rather more soluble in hot, water, and readily soluble in alcohol. The *calcium* salt, $Ca(C_{15}H_{25}O_3)_2 + 5H_2O$, crystallises in long, white, silky needles melting at 250°, and is very slightly soluble in cold water, very soluble in dilute, boiling alcohol. The *silver*, *sodium*, and *ammonium* salts are also crystalline. The white oil from which the acid has been extracted, when distilled with steam, yields a colourless, liquid, sesquiterpenic alcohol, *caparrapiol*, $C_{15}H_{26}O$; it has a sp. gr. 0·9146, a rotatory power $[a]_D = -18·58°$, refractive index 1·4843, and boils at 260° under 757 mm. pressure. When distilled with phosphoric or acetic anhydride, it is converted into the corresponding hydrocarbon, *caparrapene*, $C_{15}H_{24}$, a colourless liquid which boils at 240—250° and has a sp. gr. 0·9019 at 16°, a rotatory power $[a]_D = -2·21°$, and refractive index 1·4953; its solution in acetic acid gives a rose coloration, changing to intense violet on the addition of a trace of sulphuric acid. The residue from the steam-distillation of the white oil, constituting nearly three-fourths of the whole, is a very thick, yellowish liquid of sp. gr. 0·9751 at 18°, and rotatory power $[a]_D = +3·33°$; it contains oxygen.

The black oil, when treated with alkalis, yields a resinous acid of disagreeable odour which is not improbably a decomposition product of the crystalline acid contained in the light coloured oils. After removal of this acid, the oil has a sp. gr. 0·9319, a rotatory power $[a]_D = +6·43°$, and a refractive index 1·4811; on distillation, it yields 35·8 per cent. of caparrapiol.

N. L.

Essential Oil of Cochlearia Officinalis. By JOHANNES GADAMER (*Arch. Pharm.*, 1899, **237**, 92—105. Compare Hofmann, Abstr., 1874, 792).—The dried plant (*sine floribus*) was cut up, macerated with water, with the addition of 1/5 of its weight of flour of white mustard, and distilled with superheated steam; from 28 kilos. of the dried scurvy grass, 66 grams of oil were obtained. From a sample of the green plant, no oil could be obtained, but the plant had already flowered, and fermentation had set in by the time it was received. The oil boiled at 150—162°, and the two fractions, boiling at 150—154° and 154—156°, were found to be the purest, being practically pure secondary butylthiocarbimide, C_4H_9NCS; they had respectively the sp. gr. 0·94328 and 0·94279 at 20°/20°, molecular rotation $[M]_D = +59·12°$ and $+61·15°$, and index of refraction 1·4923 and 1·4925 at 22°. The amount of thiocarbimide was estimated by dissolving a weighed quantity of the oil in alcohol, adding excess of N/10 silver nitrate solution, allowing the whole to remain for 24 hours in a well-stoppered bottle, filtering from the precipitated silver sulphide, and titrating the excess of silver with ammonium thiocyanate solution. The fractions of the oil of higher boiling point had a rather larger rotation and lower sp. gr.; possibly they contained a little *d*-limonene.

Secondary butylthiocarbamide, $NH_2 \cdot CS \cdot NH \cdot C_4H_9$, obtained by treating the oil with ammonia, forms monoclinic crystals, and at 20° has a molecular rotation $[M]_D = +30·06°$ to 30·27° in alcoholic solution of about 3·5 per cent. strength, and 44·15° in 1 per cent. aqueous solution. When the oil is heated with twice its volume of water for 8—10 hours at 200°, a little secondary butylamine is formed, but the main product is a d.d-*dibutylthiocarbamide*, $CS(NH \cdot C_4H_9)_2$, in which both the secondary butyl groups are dextrorotatory; this melts at 108—110°, and has a molecular rotation $[M]_D = +77·08°$ at 17° in 3·3 per cent. alcoholic solution. The r.d-isomeride, obtained by the action of inactive, or racemic, secondary butylamine on active secondary butyl thiocarbamide, melts at 102—102·5°, and has a molecular rotation $[M]_D = +34·84°$ under the same circumstances, being considerably less than half the value when both butyl groups are optically active.

The further action of water on the d.d-compound produces secondary butylamine; the compound is heated with 5 times its weight of water for 15 hours at 200°—for a time at 240°. This amine is optically inactive; attempts to decompose it into its active components have been hitherto unsuccessful. Two *aurichlorides* were obtained from it, however; the less soluble crystallises with $1H_2O$ and melts at 50—52°, when anhydrous at 110°; the other forms anhydrous crystals and melts at about 150°.   C. F. B.

Essential Oils of Geranium, Citronella, and Roses. By JULIAN FLATAU and HENRI LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], **19**, 635—636).—The geraniol and citronellol in (1) Indian geranium oil, (2) Réunion geranium oil, (3) rose oil, and (4) citronella oil have been determined by the method previously described (Abstr., 1898, i, 618), with the following results:—

	1.	2.	3.	4.
Geraniol, per cent. ...	63	70	70	40
Citronellol ,,	11	10	15	6

                                                            N. L.

Essential Oil of Melissa. By JULIAN FLATAU and HENRI LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], **19**, 636—637).—A specimen of oil of melissa (balm) was found to contain 20 per cent. of geraniol, 12 per cent. of linalool, and about 6 per cent. of citronellol. N. L.

Essential Oil of Origanum Majorana. By WILHELM BILTZ (*Ber.*, 1899, **32**, 995—999).—The crude oil used in the research had a sp. gr. 0·898 at 14°/14°, a refractive index n_D 1·47738 at 14·5°, and rotation $a_D = +15°$ 45′ (100 mm.) at 15°. Fractional distillation under reduced pressure gave a fraction boiling at 77—81° under 30 mm. pressure and having the composition $C_{10}H_{16}$, whilst the last fraction boiled at 117—119° under 30 mm. pressure and had the composition $C_{10}H_{18}O$; the remaining fractions were intermediate in composition and in boiling point. The terpene fractions, when distilled from sodium, boiled at 64—74° under 20 mm. pressure, and were found to consist largely of terpinene, which was identified by the formation of the nitrosite ; a determination of the molecular weight of the fractions of highest boiling point showed that sesquiterpenes were not present in any large quantity ; about two-fifths of the oil consists of terpenes. The presence of terpineol was shown by oxidation, when Wallach's trihydroxyhexahydrocymene, $C_{10}H_{17}(OH)_3$, and the ketolactone, $C_{10}H_{16}O_3$, were isolated (Abstr., 1893, i, 597). Hydrolysis with potassium hydroxide showed the presence of 6 per cent. of ethereal salts reckoned as terpinylic acetate and the characteristic odour of the oil disappeared. The presence of acetic acid was proved, but other acids also appear to be present. T. M. L.

Essential Oil of Tropæolum Majus. By JOHANNES GADAMER (*Arch. Pharm.*, 1899, **237**, 111—120).—When this plant, in the green state, is minced in a mincing machine and distilled with steam in a vessel which may be of metal provided that it is well-tinned inside, an oil can be extracted from the distillate with ether, and this oil is benzylthiocarbimide, as it has the smell characteristic of thiocarbimides, and yields benzylthiocarbamide when it is dissolved in alcohol and treated with 30 per cent. ammonia. From 14 kilos. of the plant, 5 grams of oil, containing 86 per cent. of benzylthiocarbimide, were obtained. Hofmann (Abstr., 1874, 793) did not obtain any thiocarbimide, but benzylic cyanide instead ; this is probably because he distilled the plant without crushing it first, and the thiocarbimide is formed only by the action of an enzyme on a glucoside, contained in different cells of the plant ; the enzyme was destroyed before it could act on the glucoside, and the latter then yielded benzylic cyanide as a product of decomposition.

Attempts to isolate the glucoside have been so far successful that a neutral aqueous solution of it, almost free from foreign matter, has been obtained. On the addition of silver nitrate to this solution, a white precipitate is formed and the solution becomes acid ; the precipitate dissolves in ammonia, but crystals of a compound, $CH_2Ph\cdot NCS, Ag_2SO_4, 2NH_3$, separate almost immediately from the solution. (This is quite analogous to what happens with the glucosides of black and white mustard ; Abstr., 1897, i, 254, 360). Hydrochloric acid decomposes the silver precipitate, forming silver

chloride, sulphur, and benzylic cyanide. To it and the hypothetical glucoside the following formulæ are assigned :—

$$CH_2Ph \cdot N\!:\!C\!<^{O \cdot SO_2 \cdot OAg}_{SAg} \qquad CH_2Ph \cdot N\!:\!C\!<^{O \cdot SO_2 \cdot OK}_{S \cdot C_6H_{12}O_5} + xH_2O.$$
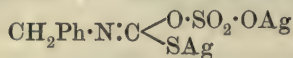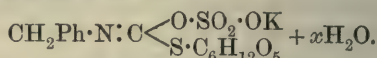
Silver salt (tropæolate).   Glucoside (glucotropæolin).

The author proposes that this glucoside should be named *gluco-tropæolin*, that the monobasic acids of which this and the sinigrin and sinalbin of black and white mustard are the salts should be called glucotropæolic, glucosinigric and glucosinalbic acids respectively, whilst to the dibasic acids obtained from these by the loss of glucose the names tropæolic, sinigric, and sinalbic acids are assigned.

C. F. B.

Empyreaumatic Oil of Juniper. By CATHELINEAU and JEAN HAUSSER (*Bull. Soc. Chim.*, 1898, [iii], 19, 577—580).—From 400 c.c. of empyreaumatic oil of juniper, by treatment with 5 per cent. aqueous soda, followed by various processes of extraction and distillation which are described in detail in the paper, the following products were obtained : *Soluble in soda.*—Extracted by light petroleum, 9 c.c. ; extracted by amylic alcohol, 36 grams ; oil volatile with steam, 6 c.c. ; resin, 19 grams ; soluble oil not volatile with steam, 4 c.c. ; soluble acids volatile with steam, 3 c.c. *Insoluble in soda.*—Distilling between 100° and 245°, 3 c.c. ; 245° and 260°, 120 c.c. ; 265° and 285°, 140 c.c. ; residue, 50 c.c. The 9 c.c. of oil extracted by light petroleum from the portion soluble in soda was similar to the portion insoluble in soda, and yielded, on distillation between 245° and 265°, 4 c.c. ; 265° and 285°, 3 c.c. ; residue, 2 c.c.

N. L.

Constitution of the Campholenic Acids and their Derivatives. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1898, [iii], 19, 565—573).—The author discusses minutely the reactions, and more especially the behaviour on oxidation, of a-campholenic acid, $CH_2\!<^{CMe_2 \cdot C\!:\!CH_2}_{CH_2-CH \cdot CH_2 \cdot COOH}$; β-campholenic acid, $CH_2\!<^{CMe_2 \cdot CMe}_{CH_2-C \cdot CH_2 \cdot COOH}$, and the isomeric lactone, $CH_2\!<^{CMe_2 \cdot CMe \cdot O \cdot CO}_{CH_2-CH--CH_2}$, with a view to showing that the known facts are in full accordance with these formulæ for the compounds.

N. L.

Constitution of Camphoric Acid and Camphor. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1898, 19, [iii], 462—469).—A theoretical paper discussing the bearing of recent researches on the author's formula for camphoric acid and on the constitution of camphor.

G. T. M.

Constitution of Isolauronolic Acid and Camphoric Acid. By G. BLANC (*Bull. Soc. Chim.*, 1898, 19, [iii], 533—537. Compare Abstr., 1897, i, 538, 554; this vol., i, 443).—The acid $C_8H_{14}O_3$, obtained by oxidising isolauronolic acid with chromic acid mixture, yields aa-dimethylglutaric acid on treatment with sodium hypobromite, and

is identical with 3-dimethylhexan-2-onoic acid (γ-acetyldimethylbutyric acid), $CMe_2Ac \cdot CH_2 \cdot CH_2 \cdot COOH$, prepared by Tiemann (Abstr., 1897, i, 200). Isolauronolic acid should accordingly be represented by one of the following formulæ :

$$COOH \cdot CH \big< {CH_2 \cdot CMe_2 \atop CH = CMe} \quad \text{or} \quad COOH \cdot C \big< {CMe \cdot CMe_2 \atop CH_2 \cdot CH_2},$$
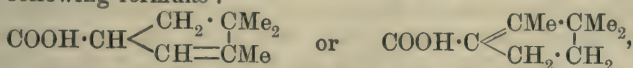
and since it is optically inactive, the latter is more probable. In accordance with this view, camphoric acid should have the constitu-

tion indicated by $CH_2 \big< {CMe_2 \cdot CMe \cdot COOH \atop CH_2 - CH \cdot COOH}$, which is identical with

that deduced by Bouveault (compare Perkin, Trans., 1898, **71**, 796).

G. T. M.

Constitution of Camphoric Acid. By LUIGI BALBIANO (*Ber.*, 1899, **32**, 1017—1023. Compare Abstr., 1897, i, 626).—The oxidation of camphoric acid by means of cold alkaline potassium permanganate to the acid $C_8H_{12}O_5$ and oxalic acid is most readily explained by means of Bredt's formula :

$$CMe_2 \big< {CH(COOH) - CH_2 \atop CMe(COOH) \cdot CH_2} \quad \rightarrow \quad CMe_2 \big< {CH(COOH) - \atop CMe(COOH) -} \big> O.$$
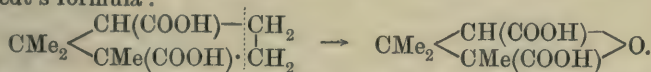
If the Perkin-Bouveault formula (this vol., i, 300) be used, it is necessary to assume the intermediate formation of trimethylglutaric acid ; the author now shows that this acid does not appear among the oxidation products, and that it is not oxidised by alkaline permanganate to the acid $C_8H_{12}O_5$; the only oxidation product appears to be a little dimethylsuccinic acid, and the greater part of the acid is not attacked. Perkin's formula does not allow of the formation of the acid $C_8H_{12}O_5$.

The acid obtained by oxidation is inactive ; it gives a *strychnine* salt which melts at 205—206° when recrystallised eight times from alcohol. When decomposed with alkali, a *dextrorotatory* acid is obtained which melts at 119°, and has $[a]_D = +5 \cdot 48°$, whilst the mother liquors gave a *lævorotatory* fraction melting at 117—119°, and having $[a]_D = -3 \cdot 35°$. The formation of a racemic mixture is regarded by the author as evidence in favour of Bredt's formula for camphoric acid, since this represents both asymmetric carbon atoms as being attacked in the oxidation.

T. M. L.

Crystalline Constituents of Galanga Root. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1899, **32**, 861—863).—The crystalline constituents of Galanga root have been investigated by Jahns (Abstr., 1882, 208, 866), who isolated three compounds which were termed campheride, galangin, and alpinin. The first named substance, which has the empirical formula $C_{16}H_{12}O_6$, crystallises from methylic alcohol in lustrous, golden needles a centimetre in length ; it contains 1 mol. of the solvent, which is removed at 100°, and melts at 227—229°. The *triacetyl* derivative crystallises from alcohol in pale yellow needles, and melts at 193—195°. When the substance is heated with methylic alcohol, potassium hydroxide, and methylic iodide, the *dimethoxymethyl* derivative is produced, along with two *compounds* melting at 154—155° and 138—140° respectively ;

the dimethoxymethyl derivative crystallises from methylic alcohol in rectangular plates and melts at 178°.   M. O. F.

Aloin. By O. A. OESTERLE (*Arch. Pharm.*, 1899, **237**, 81—92). —Aloin was dissolved in 96 per cent. alcohol, strong hydrochloric acid added, and the mixture heated in a reflux apparatus for 18—24 hours on the water-bath, and then set aside for days, or even weeks. The brownish deposit was extracted with toluene, the solution boiled with animal charcoal, and the dissolved substance crystallised alternately from toluene and acetic acid. It melts at 224°, is orange in colour, has the composition $C_{15}H_{10}O_5$, and appears to be identical with the aloe-emodin prepared from Barbados aloes (Tschirch and Pedersen, Abstr., 1898, i, 599), which, when purified as just described, melts at 223—224°. Both substances give the same absorption spectra, and both yield yellow *diacetyl* derivatives, melting at 177—178° and 175·5° respectively.

Aloin was then oxidised by adding it gradually to a mixture of potassium dichromate, water, and strong sulphuric acid heated at 80—90° (Tilden, this Journal, 1877, ii, 266); in the precipitate that formed, aloxanthin could not be found. By extracting it partially with boiling chloroform, however, finishing the extraction with toluene, and crystallising the extracted substance alternately from toluene and acetic acid, an orange-coloured substance, *alochrysin*, was obtained; this melts at 223—224°, and has the composition $C_{15}H_8O_5$. Its absorption spectrum, which is described in detail, resembles that of aloxanthin; a yellowish *acetyl* derivative melting at 245° was prepared, but not analysed.   C. F. B.

Absinthin. By PAUL BOURCET (*Bull. Soc. Chim.*, 1898, **19**, [iii], 537—539. Compare Abstr., 1892, 1240). The method of separating absinthin from the leaves of *Artemisia absinthium* is fully described. When pure, this glucoside crystallises from dilute alcohol in prismatic needles, melts at 68°, and has an extremely bitter taste. Senger's formula for absinthin, $C_{15}H_{20}O_4$ (*loc. cit.*), is confirmed.   G. T. M.

Brazilin. By W. FEUERSTEIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1899, **32**, 1024—1030).—The dimethylic ether of the oxidation product of brazilin, $C_9H_6O_4$, described by Schall and Dralle as crystallising in lustrous, yellow plates which turned white when heated with dilute nitric acid (Abstr., 1892, 502), can be obtained as a colourless, crystalline solid by boiling its alcoholic solution with animal charcoal; on treatment with an alcoholic solution of sodium ethoxide, it gives a mixture of fisetol dimethylic ether, $OH \cdot C_6H_3(OMe) \cdot CO \cdot CH_2 \cdot OMe$ [= 4 : 2 : 1], and formic acid, the former compound being identical with the substance obtained by Herzig (Abstr., 1891, i, 138) from methyl-fisetin and alcoholic potassium hydroxide, the melting points of the ethylic ether, 67—68° (Herzig, 60—62°), and the phenylhydrazone, 60—61° (Herzig 55—57°) being only slightly different. It is probable, therefore, that this oxidation product is a 3-hydroxypheno-γ-pyronol

$$OH \cdot C_6H_3 \underset{O-CH}{\overset{CO \cdot C \cdot OH}{<}} \quad ;$$

and bearing in mind that Herzig obtained protocatechuic acid on fusing brazilin with potassium hydroxide, the

following modification of Schall and Dralle's formula for brazilin

is the most probable, $O{<}{\substack{C_6H_3(OH)\\ CH:C(OH)}}{>}CH{\cdot}CH_2{\cdot}C_6H_3(OH)_2$.

Brazilein, which is formed from brazilin by the elimination of 2 atoms of hydrogen, can then either have the paraquinonoid structure which would be formed by the elimination of the two hydrogen atoms marked (*) in the above formula, or the non-quinonoid formula,

$$O{<}{\substack{C_6H_3(OH)\\ CH_2{-}CO}}{>}C{:}CH{\cdot}C_6H_3(OH)_2,$$
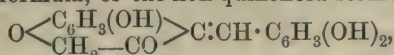
and since there are already orange dyes known (Abstr., 1896, i, 606) containing the chromophor $CO{\cdot}C{:}C$, and it has been shown that the nearer the auxochrome is to the chromophore the more intense the colour, and further that the acidic methylene group, CH_2, can act as an auxochrome, it is not at all unlikely that the acidic methylene group in this formula for brazilein acting as the auxochrome is sufficient to change the colour from orange to red. J. F. T.

Constitution of Brazilin. By CARL SCHALL (*Ber.*, 1899, **32**, 1045—1046).—The formula suggested by Feuerstein and von Kostanecki (compare preceding abstract) is, in the author's opinion, the correct one. J. F. T.

NOTE.—This formula is very similar to that recently proposed by Gilbody and Perkin (Proc., 1899, 75), in which the protocatechuic nucleus is attached to the γ-pyrone ring in the ortho-position relatively to the pyrone oxygen. J. F. T.

Pyrrolidine. By JULIUS SCHLINCK (*Ber.*, 1899, **32**, 947—958. Compare Ciamician and Magnaghi, Abstr., 1885, 1243; Ladenburg, *ibid.*, 1886, 528; 1887, 1052; Gabriel, *ibid.*, 1892, 131).—Various attempts have been made to obtain good yields of pyrrolidine by different methods, but without success.

γ-*Methoxybutyronitrile*, $OMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN$, obtained by the action of methylic alcohol and potassium cyanide on methoxychloropropane (Perkin, Trans., 1894, **65**, 596), is an oily liquid which distils at 172—175°, and when reduced with sodium and methylic alcohol yields δ-*methoxybutylamine*; this, when dried over solid potassium hydroxide, forms a clear liquid boiling at 142—145° and having a strongly alkaline reaction; the *hydrochloride* is extremely hygroscopic and readily soluble in alcohol, and the *platinochloride*, $(C_5H_{13}NO)_2,H_2PtCl_6$, crystallises in glistening, golden plates decomposing at 175° without melting. The base combines with phenylthiocarbimide, yielding *phenyl-δ-methoxybutylthiocarbamide*, $NHPh{\cdot}CS{\cdot}NH{\cdot}C_4H_8{\cdot}OMe$, which crystallises from water in glistening plates or prisms melting at 70·5°. As the yield of methoxybutylamine is little or no better than that of the phenoxy-compound (Gabriel, *loc. cit.*), no attempt was made to convert it into pyrrolidine.

When sodium paratolyloxide is boiled for 1½ hours with an alcoholic solution of chlorobutyronitrile, it yields γ-*paratolyloxybutyronitrile*, $C_7H_7O{\cdot}C_3H_6{\cdot}CN$, a yellowish oil distilling at 296—298° and solidifying in small plates melting at 17—18°; when hydrolysed with concentrated

hydrochloric acid, the nitrile yields *paratolyloxybutyric acid*, which crystallises from light petroleum in glistening plates melting at 87°, and when reduced with sodium and alcohol is converted into δ-*paratolyloxybutylamine*, which is a colourless oil with a disagreeable odour and boils at 262—271°. ¡ The *hydrochloride* of this base crystallises in needles, the *platinochloride*, $(C_{11}H_{17}NO)_2,H_2PtCl_6$, in large, yellow, rhombic prisms melting and decomposing at 216°, the *aurichloride*, $C_{11}H_{17}NO,HAuCl_4$, in golden-yellow plates and prisms decomposing at 73°; the *dichromate*, $(C_{11}H_{18}NO)_2Cr_2O_7$, begins to melt at 80° and is completely decomposed at 122°; the *picrate* forms long, yellow needles melting at 151—152°. The base combines with phenylthiocarbimide, yielding *phenyl paratolyloxybutylthiocarbamide*, which crystallises from alcohol in indented needles melting at 107·5—109°; when heated for 10 hours at 100° with concentrated hydrochloric acid, the base is converted into δ-chlorobutylamine, and this may then be converted into pyrrolidine, but the yield is practically the same as by Gabriel's method.

The reduction of succinimide by the aid of amylic alcohol and sodium in place of ethylic alcohol (Ladenburg) leads to the formation of only minute traces of pyrrolidine; the reduction of pyrrolidone (Gabriel, Abstr., 1890, 360) and of pyrroline do not give any better yield.

1-*Benzylpyrrolidine*, $C_4NH_8 \cdot C_7H_7$, is readily obtained by the action of benzylic chloride on pyrrolidine as a clear, oily liquid of faint, disagreeable odour boiling at 237°, its *hydrochloride* crystallises from a strongly acid solution in large, rhombic, deliquescent plates; the *platinochloride* forms yellowish-red needles melting and decomposing at 156°, the *aurichloride* crystallises in lemon-yellow needles melting and decomposing at 120°, the *picrate* is readily soluble in water or alcohol, and melts at 128°. The base itself readily combines with methylic iodide, forming a quaternary ammonium compound,

$$C_7H_7 \cdot C_4NH_8MeI,$$
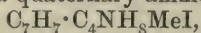
which is readily soluble in acids, water, or alcohol; the *picrate* melting at 119°, the *platinochloride*, $(C_{12}H_{17}N)_2,H_2PtCl_6$, melting at 183—184°, and the *aurichloride* melting at 90·5°, have been prepared.

Paranitrobenzylpyrrolidine, obtained by the action of paranitrobenzylic chloride on an alcoholic solution of pyrrolidine at 100°, is a somewhat pleasant smelling oil which cannot be distilled without undergoing decomposition; the *picrate* crystallises in slender, lemon-yellow needles melting at 151—153°, the *platinochloride* melts and decomposes at 160°, and the *aurichloride* at 155°. *Orthonitrobenzylpyrrolidine* also forms a yellowish oil which undergoes decomposition when distilled; its *aurichloride* crystallises in slender, golden-yellow prisms melting and decomposing at 160°, and readily soluble in ether but sparingly so in water; its *picrate* melts at 152·5°.

Pyrrolidine reacts with both aliphatic and aromatic thiocarbimides, yielding well defined crystalline derivatives, of which the following have been examined: *Pyrrolidinephenylthiocarbamide*,

$$C_4NH_8 \cdot CS \cdot NHPh,$$
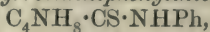
crystallises from hot water in needles or rhombic plates melting at

148·5°. *Pyrrolidinemethylthiocarbamide* forms long needles melting at 117°; the *ethyl* compound melts at 91°, the *allyl* compound sinters and then melts at 70°.

Pyrrolidineallyl-ψ-thiocarbamide, $\begin{array}{c}\text{CHMe·S}\\|\\\text{CH}_2\text{---N}\end{array}{>}\text{C·N}{<}\begin{array}{c}\text{CH}_2\text{·CH}_2\\\text{CH}_2\text{·CH}_2\end{array}$ (compare Gabriel, Abstr., 1889, 848; 1890, 127), formed when pyrrolidineallyl-thiocarbamide is heated with fuming hydrochloric acid for 2 hours at 100°, is a yellowish oil sparingly soluble in water which yields an *aurichloride* melting at 107—108° and a *platinochloride* melting and decomposing between 182° and 201°.

1-γ-*Phenoxypropylpyrrolidine*, $OPh \cdot C_3H_6 \cdot C_4NH_8$, obtained by the action of pyrrolidine on γ-phenoxypropylic chloride, is a brownish oil which boils at 288·5° and yields a *platinochloride* melting and decomposing at 160—161°. When treated according to Gabriel and Stelzner's method (Abstr., 1896, i, 703), it yields γ-*bromopropyl-pyrrolidine hydrobromide*, $C_4NH_8 \cdot C_3H_6Br, HBr$, as an extremely hygroscopic solid; the *picrate* sinters at 119° and melts at 123°. Attempts to obtain trimethylene pyrrolylium bromide proved unsuccessful.

<div align="right">J. J. S.</div>

Action of αδ-Dibromopentane on Primary and Secondary Bases. By MAX SCHOLTZ and P. FRIEMEHLT (*Ber.*, 1899, **32**, 848—853).—The action of 1 : 4-dibromopentane on bases is less energetic than that of orthoxylylenic bromide (compare Abstr., 1898, i, 565), but follows the same lines.

1 : 2-*Phenylmethylpyrrolidine*, $\begin{array}{c}\text{CH}_2\text{·CHMe}\\|\\\text{CH}_2\text{---CH}_2\end{array}{>}\text{NPh}$, prepared by heating an alcoholic solution of αδ-dibromopentane with excess of aniline, is a colourless liquid boiling at 134° under 25 mm. pressure; the *platinochloride* crystallises in needles, and the *picrate* melts at 105°.

αδ-*Diorthotoluidinopentane*,

$$C_6H_4Me \cdot NH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot NH \cdot C_6H_4Me,$$

prepared by heating αδ-dibromopentane with orthotoluidine, boils at 191—193° under 23 mm. pressure; the *picrate* crystallises from alcohol in needles and melts at 147°.

1 : 2-*Paratolylmethylpyrrolidine*, $\begin{array}{c}\text{CH}_2\text{·CHMe}\\|\\\text{CH}_2\text{---CH}_2\end{array}{>}\text{N·C}_6\text{H}_4\text{Me}$, formed when paratoluidine acts on αδ-dibromopentane, is a colourless oil which boils at 147—149° under 20 mm. pressure; the *picrate* crystallises from dilute alcohol in microscopic needles and melts at 117°.

1-*Metanitrophenyl-2-methylpyrrolidine*, $\begin{array}{c}\text{CH}_2\text{·CHMe}\\|\\\text{CH}_2\text{---CH}_2\end{array}{>}\text{N·C}_6\text{H}_4\text{·NO}_2$, obtained from αδ-dibromopentane and metanitraniline, crystallises in brownish-red needles on adding petroleum to the benzene solution and melts at 140°.

αδ-*Diorthonitranilinopentane*, $C_5H_{10}(NH \cdot C_6H_4 \cdot NO_2)_2$, crystallises in orange-red needles and melts at 172°.

Pentamethylene-2-methylpyrrolidinium bromide,

$$\begin{array}{c}\text{CH}_2\text{·CHMe}\\|\\\text{CH}_2\text{---CH}_2\end{array}{>}\text{NBr}{<}\begin{array}{c}\text{CH}_2\text{·CH}_2\\\text{CH}_2\text{·CH}_2\end{array}{>}\text{CH}_2,$$
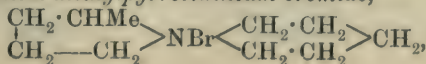
prepared by the action of alcoholic piperidine on αδ-dibromopentane, is a crystalline, hygroscopic salt; the *platinochloride* and *aurichloride* melt at 250° and 220° respectively.   M. O. F.

Perbromides of some Cyclic Acetone Bases. By A. SAMTLEBEN (*Ber.*, 1899, **32**, 663—667).—When 4-hydroxy-1 : 2 : 2 : 6 : 6-pentamethylpiperidine hydrobromide perbromide (Abstr., 1898, i, 473, where *4-hydroxy* is inadvertently omitted), is digested with aqueous sodium carbonate, hydroxypentamethylpiperidine is regenerated for the most part, but a little 1-bromo-4-hydroxy-2 : 2 : 6 : 6-tetramethylpiperidine is formed; this is interesting, as it exemplifies the formation of a secondary from a tertiary amine.

*4-Bromo-*2 : 2 : 6 : 6-*tetramethylpiperidine* is obtained by heating hydroxytetramethylpiperidine with four times its weight of fuming hydrobromic acid for an hour at 150°; it melts at 45°, and in the air undergoes a slow transformation into the hydrobromide of 2 : 2 : 6 : 6-tetramethyl-Δ_3-tetrahydropyridine (triacetonine); its *hydrobromide* forms an orange-yellow *perbromide*, $C_9NH_{18}Br\cdot Br_2$, when dissolved in cold, dilute hydrobromic acid and treated with bromine; this loses its bromine readily, and when it is stirred with dilute aqueous sodium carbonate forms yellow 1 : 4-*dibromo-*2 : 2 : 6 : 6-*tetramethylpiperidine,* which melts at 45°.

4-Iodo-2 : 2 : 6 : 6-tetramethylpiperidine, which can be obtained from the 4-hydroxy-compound and hydriodic acid at 150°, forms an orange-yellow hydrobromide perbromide, and by the action of sodium carbonate on this, 1-*bromo-4-iodo-*2 : 2 : 6 : 6-*tetramethylpiperidine* is obtained; it melts at 98°, and loses its bromine when boiled with acids, but not with alkalis or water.

2 : 2 : 6 : 6-Tetramethyl-Δ_3-tetrahydropyridine hydrobromide yields an orange-red *perbromide* when treated with bromine at the ordinary temperature; this melts at about 55°, and at a higher temperature undergoes a molecular transformation into 3 : 4-*dibromo-*2 : 2 : 6 : 6-*tetramethylpiperidine,* which decomposes at 170°; the base corresponding with this could not be isolated, as alkalis remove all the bromine, regenerating Δ_3-tetrahydropyridine.   C. F. B.

Stereochemistry of Quinquevalent Nitrogen. Quadrivalent Sulphur. By OSSIAN ASCHAN (*Ber.*, 1899, **32**, 988—994. Compare Wedekind, this vol., i, 351, and Marckwald and Droste-Huelshoff, *ibid.*, 326).—*Diethylenedipiperidyl iodide,* $C_5H_{10}NI\cdot(C_2H_4)_2\cdot NC_5H_{10}I$, crystallises from water in brownish, glistening flakes, and melts at 295°; like the bromide, it is only known in one form. *Propylenedipiperidide,* $C_5H_{10}N\cdot CHMe\cdot CH_2\cdot C_5H_{10}N$, boils at 265—266°, and, when combined with ethylenic dibromide, gives an *ethylenepropylenedipiperidyl bromide* different from that which is obtained by the interaction of ethylene dipiperidide and propylenic bromide.

Ethylenedipiperidyl dimethiodide exists in two triclinic modifications [$a : b : c = 1\cdot887 : 1 : 0\cdot429$, $a = 88°\ 42'$, $\beta = 88°\ 55\frac{1}{2}'$, $\gamma = 100°\ 45'$; $a : b : c = 1\cdot012 : 1 : 0\cdot809$, $a = 80°\ 22\frac{1}{2}'$, $\beta = 79°\ 49'$, $\gamma = 95°\ 41'$], of which the latter has the higher melting point by 3°. These are both produced by the action of methylic iodide on ethylenedipiperidide, together

with a little of the *monomethiodide* melting at 155·5°, and are regarded as analogous to racemic and mesotartaric acids.

The additive compounds of methylenic and ethylenic iodides and ethylenic bromide with methylic ethylic sulphide have also been prepared, in order to establish, if possible, the existence of racemic and meso-forms.   T. M. L.

Action of Alkylic Iodides on Indoles. 2′: 3′: 3′-Trimethyl-indolenine. By GIUSEPPE PLANCHER and D. BETTINELLI (*Gazzetta*, 1899, 29, i, 106—120. Compare Abstr., 1898, i, 536).—In preparing 2′: 3′: 3′-trimethylindolenine by the condensation of methyl isopropyl ketone with phenylhydrazine in presence of zinc chloride, the latter forms, with the base, a double compound, which the authors have now shown to have the composition $ZnCl_2(C_{11}H_{13}N)_2$. The free trimethyl-indolenine produces in benzene solution the normal depression of freezing point. A small quantity of an indole formed in the above condensation proves to be 2′: 3′-dimethylindole.

2′: 3′: 3′-Trimethylindolenine forms a *benzoyl* derivative, $C_{11}H_{13}NBz$, which crystallises from alcohol in white needles melting unchanged at 183°, is almost insoluble in benzene or light petroleum, has the normal molecular weight in bromoform solution, is stable towards permanganate, and is readily hydrolysed by acids or alkalis.

3′: 3′-*Dimethylindolenine-2′-formoxime*, $C_6H_4\underset{CMe_2}{\overset{N}{<}}C\cdot CH:NOH$,

prepared by acting on an acetic acid solution of the trimethylindolenine with cold potassium nitrite solution, crystallises from a mixture of benzene and light petroleum in white needles or prisms melting at 156°. It is soluble in caustic alkalis, and is reprecipitated by carbonic anhydride. On heating with excess of acetic anhydride, it gives rise to 3′: 3′-dimethylindolenine-2′-formonitrile, $C_6H_4\underset{CMe_2}{\overset{N}{<}}C\cdot CN$, which is a colourless oil having a pleasant smell, boils at 150—151° under 30 mm. pressure, and is soluble in the ordinary organic solvents. When heated with hydrochloric acid, this nitrile yields the 3′: 3′-dimethylindolinone obtained by Brunner (Abstr., 1897, i, 438); this crystallises from ethylic acetate in orthorhombic crystals [$a : b : c = 0·8521 : 1 : 0·7212$]. Brunner's compound gave [$a : b : c = 0·8496 : 1 : 0·7219$].

When trimethylindolenine is oxidised with permanganate, it yields a small quantity of an acid melting at 140°, the constitution of which was not determined. On reduction with tin and hydrochloric acid, the secondary trimethylindoline prepared by Ferratini (Abstr., 1894, i, 96) is obtained.   T. H. P.

Action of Alkalis on Orthomethyldiazonium Salts. By EUGEN BAMBERGER (*Annalen*, 1899, 305, 289—370).—It has been shown that, under certain conditions (Abstr., 1896, i, 300), alkalis convert diazonium salts into the highly explosive diazo-anhydrides, in accordance with the equation $2Arr\cdot N_2\cdot Cl + 2NaOH = 2NaCl + H_2O + (Arr\cdot N_2)_2O$ [Arr. is an abbreviation of arryl, which term the author now employs to express univalent aromatic radicles]; the action is

not general, however, and does not apply to 2 : 4 : 6-tribromodiazo-benzene, which yields 3 : 5-dibromo-2-diazo-1-phenol, $C_6H_2Br_2\!<\!^O_N\!>\!N$.

Orthodiazotoluene gives rise to indazole, $C_6H_4\!<\!^{CH}_N\!>\!NH$, described by Fischer and Tafel, whilst diazomesidine yields 1 : 3-dimethyl-indazole, along with an orange-yellow compound having the empirical formula $C_{18}H_{20}N_4$, and probably representing the mesitylazo-derivative of the dimethylindazole ; the bye-products which accompany the formation of these two substances are mesitol, mesitylene, chloromesitylene, mesidine, and mesitylenic acid.

1 : 3-*Dimethylindazole*, $C_6H_2Me_2\!<\!^{CH}_N\!>\!NH$, prepared from diazo-mesidine and caustic soda under conditions described in the original paper, crystallises from a mixture of benzene and petroleum in slender, white needles melting at 133—134° ; the *acetyl* derivative crystallises from alcohol in white needles, and melts at 116—117°.

3′-*Mesitylazo*-1:3-*dimethylindazole*, $C_6H_2Me_2\!<\!^{C(N_2 \cdot C_6H_2Me_3)}_N\!>\!NH$,

crystallises from alcohol or glacial acetic acid in lustrous, orange-yellow needles melting at 258°, and subliming in very slender, sulphur-yellow needles ; the solution in concentrated sulphuric acid is bluish-violet, becoming cherry-red when treated with a nitrate or a nitrite. The substance is formed, not only in the manner described above, but also by the action of diazotised mesidine on dimethylindazole. Reduction with stannous chloride, or with alcoholic ammonium sulphide, resolves the azo-compound into mesidine and

3′-*amido*-1 : 3-*dimethylindazole*, $C_6H_2Me_2\!<\!^{C(NH_2)}_N\!>\!NH$, which crys-tallises from a mixture of benzene and petroleum in slender, white needles and melts at 150—151° ; this base dissolves somewhat readily in water, the solution giving characteristic precipitates with solutions of metallic salts, and developing a reddish-violet coloration when agitated with sodium hydroxide. Mesitylazodimethylindazole yields dimethylindazole, mesidine, and ammonia when reduced with sodium in ethylic alcohol.

3′-*Benzeneazo*-1 : 3-*dimethylindazole*, $C_6H_2Me_2\!<\!^{C(N_2Ph)}_N\!>\!NH$, pre-pared by the action of diazotised aniline on dimethylindazole, crystal-lises from benzene in concentric aggregates of golden-yellow needles, and melts at 206·5—207·5°.

The *benzylidene* derivative of 3′-amido-1 : 3-dimethylindazole crystal-lises from benzene or alcohol in colourless needles and melts at 183·5—184·5° ; the *thiocarbamide* derivative, $C_6H_2Me_2\!<\!^{C-NH}_N\!>_N\!>\!CS$,

crystallises from petroleum in slender, pale yellow needles, and melts at 208—209°. The *benzenesulphonamide* crystallises from dilute alcohol in lustrous, rectangular leaflets and melts at 232—233°. The *diazo-*

hydroxide, prepared by diazotising the base in presence of the minimum quantity of mineral acid, decomposes at 130°, and dissolves sparingly in water, forming dimethylindazoletriazoline; the solution in hydrochloric acid contains dimethylindazoletriazoline hydrochloride, whilst the alkaline solutions consist of normal alkali dimethylindazolediazotates.

Dimethylindazoleazo-β-naphthol, $C_6H_2Me_2 \begin{array}{c} C(N_2 \cdot C_{10}H_6 \cdot OH) \\ | \\ N \end{array}\!\!\!\!> NH$,

prepared from diazotised amidodimethylindazole and the naphthol, crystallises from xylene in bronze-coloured needles with greenish-gold reflex; it melts at 266—267° when quickly heated, and forms an indigo-blue solution in sulphuric acid, changing to magenta-red when treated with a crystal of nitre.

3-*Chloro*-1:3-*dimethylindazole*, $C_6H_2Me_2 \begin{array}{c} CCl \\ | \\ N \end{array}\!\!\!> NH$, prepared by

heating amidodimethylindazole diazohydroxide with concentrated hydrochloric acid in a reflux apparatus, sublimes in slender needles and melts at 174°.

1:3-*Dimethyl*-4'-*hydroxy*-β-*phenotriazine*, $C_6H_2Me_2 \begin{array}{c} C(OH) \\ \| \\ N=N \end{array}\!\!\!\!> N$, ob-

tained by oxidising amidodimethylindazole with hydrogen peroxide, crystallises from benzene in aggregates of slender, lustrous needles and melts at 219—220°, yielding gas.

[With ANTON VON GOLDBERGER.] — 3'-*Orthotolueneazoindazole*,

$C_6H_4 \begin{array}{c} C(N_2 \cdot C_6H_4Me) \\ | \\ N \end{array}\!\!\!\!> NH$, a bye-product in the formation of in-

dazole on treating diazotised orthotoluidine with sodium hydroxide, is also obtained by combining indazole with diazotoluidine; it crystallises from boiling xylene in slender, orange-yellow needles and melts at 211—211·5°.

3'-*Benzeneazoindazole*, $C_6H_4 \begin{array}{c} C(N_2Ph) \\ | \\ N \end{array}\!\!\!> NH$, prepared from diazo-

nium chloride and indazole, also crystallises from xylene in orange-yellow needles, and melts at 185·5—186°.

3'-*Amidoindazole*, $C_6H_4 \begin{array}{c} C(NH_2) \\ | \\ N \end{array}\!\!\!> NH$, obtained by reducing the

foregoing azo-compound with ammonium sulphide, crystallises slowly from a mixture of ether and benzene in beautiful, highly lustrous, monoclinic prisms melting at 153·5—154·5°; an intense red coloration is developed when sodium hydroxide is added to the aqueous solution exposed to air or in presence of potassium ferricyanide. Characteristic results are obtained on treating the aqueous solution of amidoindazole with Fehling's solution, and with solutions of silver nitrate, bleaching powder, ferric chloride, and chromic acid. The *sulphate* crystallises in needles, and melts at 223—224°; the *oxalate*, *picrate*, and *hydrochloride* are also crystalline. The *diacetyl* derivative crystallises from dilute alcohol in silky, white needles and melts at 177—178°; the *dibenzoyl* derivative separates from xylene in lustrous, transparent needles and melts at 182°. The *paranitrobenzylidene* derivative melts

at 232—234°. When amidoindazole is reduced in alcoholic solution with sodium, indazole is formed.

Diazoindazole hydroxide, $C_6H_4 <^{C(N:NOH)}_{N}> NH$, precipitated when a 10 per cent. solution of sodium nitrite is added to amidoindazole dissolved in 2 per cent. hydrochloric acid, decomposes at 128°. It closely resembles the dimethylic derivative in chemical behaviour, and yields indazoletriazoline when treated with boiling water during a few minutes; protracted action, however, converts it into a crystalline substance which is volatile in steam and soluble in aqueous sodium hydroxide, probably consisting of the corresponding phenol.

Indazoleazo-β-naphthol, $C_6H_4 <^{C(N_2 \cdot C_{10}H_6 \cdot OH)}_{N}> NH$, prepared from diazoindazole hydroxide and β-naphthol, crystallises from amylic alcohol or from xylene in slender, deep red needles, and melts at 250—251°.

Diazoamidoindazole, $C_7H_5N_2 \cdot N:N \cdot NH \cdot C_7H_5N_2$, obtained on adding diazotised amidoindazole to a solution of the base in hydrochloric acid, forms a dark yellow, amorphous powder, and decomposes at 183°; aqueous sodium hydroxide develops a green coloration, which becomes red, and then brown, an odour of nitrobenzene being ultimately produced.

3′-Chlorindazole, $C_6H_4 <^{C Cl}_{N}> NH$, prepared from amidoindazole by the Sandmeyer reaction, crystallises from water or from petroleum in very long, silky needles, and melts at 148—148·5°; it is acidic in character, being soluble in cold, dilute aqueous sodium hydroxide. Mercuric chloride and silver nitrate yield sparingly soluble double salts, and bromine water produces a white, crystalline precipitate in very dilute solutions.

4′-Hydroxy-β-phenotriazine, $C_6H_2Me_2 <^{C(OH)}_{N=N}> N$, obtained on oxidising amidoindazole with hydrogen peroxide, crystallises from water or from benzene in snow-white, lustrous needles and melts at 213°; it is identical with benzazimide, described by Weddige and Finger (Abstr., 1887, 667). Hydroxyphenotriazine is also formed by the action of ammonia on ethylic anthranilate (compare Zacharias, Abstr., 1891, 912).

3-Methylindazole, $C_6H_3Me <^{C H}_{N}> NH$, prepared by the action of sodium hydroxide on diazotised unsymmetrical metaxylidine, is identical with Gabriel and Stelzner's 3-methylindazole (Abstr., 1896, i, 320); it crystallises from water or from petroleum in white needles and melts at 114—115°.

3′-Metaxyleneparazo-3-methylindazole, $C_6H_3Me <^{C(N_2 \cdot C_6H_3Me_2)}_{N}> NH$, formed as a bye-product in the preparation of 3-methylindazole, crystallises in yellow nodules, and sublimes in bright yellow, slender needles; it melts at 228—229° and dissolves in concentrated sulphuric

acid, forming an intense violet coloration, which becomes orange-red on adding a crystal of nitre. Reduction with stannous chloride or ammonium sulphide resolves the azo-compound into $1:3:4$-xylidine and 3-*methyl*-3'-*amidoindazole*, $C_6H_3Me{<}\begin{smallmatrix}C(NH_2)\\N\end{smallmatrix}{>}NH$, which crystallises from benzene in lustrous, white leaflets and melts at $190 \cdot 5 - 191 \cdot 5°$; when the aqueous solution is agitated with sodium hydroxide in presence of air or potassium ferricyanide, a violet-red coloration is produced. Characteristic changes are brought about by Fehling's solution and by solutions of mercuric chloride, silver nitrate, picric acid, ferric chloride, and bleaching powder; alkaline permanganate is instantly reduced, and nitrous acid gives rise to the diazo-hydroxide.

3-*Methyl*-4'-*hydroxy*-β-*phenotriazine*, $C_6H_3Me{<}\begin{smallmatrix}C(OH)\\N = N\end{smallmatrix}{>}N$, produced on oxidising methylamidoindazole with hydrogen peroxide, crystallises in white needles and melts at $228°$. M. O. F.

Imidophenyltriazoline. By GEROLAMO CUNEO (*Gazzetta*, 1899, **29**, i, 12—32).—Phenylamidoguanidine hydrochloride and sodium formate, when boiled together in formic acid solution, yield a compound which is either 3-imido-1-phenyltriazoline, $NPh{<}\begin{smallmatrix}NH \cdot C:NH\\CH:N\end{smallmatrix}$, or an amidotriazole derivative, $NPh{<}\begin{smallmatrix}N = C \cdot NH_2\\CH:N\end{smallmatrix}$. To decide between these constitutions, it was methylated and acetylated, when it yielded mono- and di-derivatives in both cases; this behaviour agrees with either formula. Attempts to decompose the methyl compounds by the action of acids or alkalis gave negative results. The formation of a benzylidene derivative, although explained better by the amido-formula, does not exclude the imido-constitution, which is favoured by the formation of a nitroso-derivative with nitrous acid.

3-*Imido*-1-*phenyltriazoline* crystallises from boiling water in long, colourless, silky needles melting at $150°$, and is very soluble in alcohol or ether. Its *hydrochloride*, $C_8N_4H_8,HCl + H_2O$, is very soluble in water or alcohol, and crystallises from dilute hydrochloric acid solution in long, colourless, monoclinic needles melting at $187°$ [$a:b:c = 1 \cdot 17999 : 1 : 0 \cdot 60475$; $\beta = 82° 52'$]. The *nitrate*, $C_8N_4H_8,HNO_3$, separates from water in long, thin, colourless needles soluble in alcohol and melting at $181°$. The *picrate*, $C_8N_4H_8,C_6H_3N_3O_7$, forms yellow needles which melt at $220°$, and are soluble in water or alcohol. The *platinochloride*, $(C_8N_4H_8)_2,H_2PtCl_6 + 2H_2O$, is slightly soluble in alcohol or ether, and separates from hydrochloric acid solution in long, orange-red plates; when heated or treated with boiling water, it is converted into *tetrachloroplatinophenylimidotriazoline*, $(C_8N_4H_8)_2PtCl_4$, a pale yellow, amorphous, flocculent substance insoluble in water.

2-*Nitroso*-3-*imido*-1-*phenyltriazoline*, $C_8N_4H_7 \cdot NO$, obtained by the action of nitrous acid on phenylimidotriazoline, forms yellowish crystals and is very soluble in alcohol.

Benzylideneimidophenyltriazoline, $C_8N_4H_6:CHPh$, forms colourless crystals melting at $155°$, and is very soluble in alcohol or chloroform,

less so in ether. On boiling with water or on dissolving in cold hydrochloric acid, an odour of benzaldehyde is produced.

2-*Acetyl*-3-*imido*-1-*phenyltriazoline*, $C_8N_4H_7Ac$, obtained by the action of acetic anhydride on imidophenyltriazoline, separates from alcohol in colourless crystals melting at 168°. 2-*Acetyl*-3-*acetimido*-1-*phenyl-triazoline*, $C_8N_4H_6Ac_2$, forms colourless needles melting at 118° and dissolving readily in alcohol or carbon bisulphide.

3-*Imido*-1-*phenyl*-2-*methyltriazoline*, $C_8N_4H_7Me$, prepared by the action of methylic iodide on imidophenyltriazoline, separates as the *hydriodide*, $C_8N_4H_7Me,HI + H_2O$, which crystallises from water in broad, orange-yellow, iridescent plates, and melts at 170°; the *picrate*, $C_8N_4H_7Me,C_6H_3N_3O_7$, forms orange-red prisms melting at 184°, and dissolves sparingly in water or ether, but readily in alcohol.

3-*Methylimido*-1-*phenyl*-2-*methyltriazoline*, $C_8N_4H_6Me_2$, is an oil; its *picrate*, $C_8N_4H_6Me_2,C_6H_3N_3O_7$, crystallises in bright yellow, silky needles melting at 201° with decomposition; it is slightly soluble in ether, more so in water, and very readily in alcohol.

Bromophenylimidotriazoline, $C_8N_4H_7Br$, crystallises from alcohol in groups of beautiful, orange-yellow plates melting at 196°; it dissolves readily in alcohol or chloroform, but only slightly in water or ether.

a-*Phenylmethylsemicarbazide*, $NH_2 \cdot CO \cdot NMe \cdot NHPh$, obtained by the action of formic acid on phenylamidomethylguanidine, crystallises from water in large, colourless plates melting at 147°; it is very soluble in alcohol, ether, chloroform, or boiling water, and insoluble in carbon bisulphide. To confirm its constitution, it was prepared synthetically from cyanic acid and methylphenylhydrazine.

By reducing phenylimidourazole by means of phosphorus penta-sulphide, the same imidophenyltriazoline is obtained as results from the reaction of formic acid and phenylamidoguanidine.

T. H. P.

New Triazoline Compounds. By GEROLAMO CUNEO (*Gazzetta*, 1899, **29**, i, 89—106).—The author finds that reactions analogous to that between formic acid and phenylamidoguanidine take place with other acids, and also with other derivatives of amidoguanidine.

3-*Imido*-1-*paratolyltriazoline*, $C_7H_7 \cdot N < \begin{smallmatrix} NH \cdot C:NH \\ CH:N \end{smallmatrix}$, obtained by pro-longed boiling of a formic acid solution of equivalent quantities of paratolylamidoguanidine and dry sodium formate, crystallises in beautiful, colourless needles, melts at 185°, and is very soluble in alcohol or chloroform. Its *hydrochloride*, $C_9N_4H_{10},HCl$, forms beautiful, colourless, monoclinic needles $[a:b:c = 2\cdot19444:1:4\cdot75266 ; \beta = 72°41']$, which show signs of fusion at 225° and melt completely and decompose at 234°. It is almost insoluble in ether or chloroform, but dissolves moderately in water, and more so in alcohol. The *platinochloride*, $(C_9N_4H_{10})_2,H_2PtCl_6$, forms small, orange-coloured needles almost insoluble in alcohol or ether; when heated at 200°, it loses 2HCl very quickly, and then goes on gradually decreasing in weight.

3-*Imido*-1-*orthotolyltriazoline*, $C_7H_7 \cdot N < \begin{smallmatrix} NH \cdot C:NH \\ CH:N \end{smallmatrix}$, prepared by boiling together, in molecular proportion, orthotolylamidoguanidine

hydrochloride and dry sodium formate in glacial formic acid solution, forms beautiful, colourless, prismatic needles melting at 122°. Its *picrate*, $C_9N_4H_{10},C_6H_3N_3O_7$, separates from alcohol in beautiful, yellow, lozenge-shaped crystals melting at 192° and moderately soluble in water or alcohol.

3-*Imido*-1-*phenyl*-5-*methyltriazoline*, $NPh{<}{{NH \cdot C\!:\!NH}\atop{CMe\!:\!N}}$, produced by heating a mixture of equivalent proportions of phenylamidoguanidine hydrochloride and dry sodium acetate in presence of an excess of acetic anhydride, is only slightly soluble in ether, but more so in water, alcohol, or chloroform. It crystallises from water in beautiful, colourless, monoclinic prisms melting at 186° [$a:b:c =$ 1·28824 : 1 : 2·13496 ; $\beta = 53°\ 38'$]. Its *hydrochloride*, $C_9H_{10}N_4,HCl +$ H_2O, crystallises in cubes which are very soluble in water. The *platinochloride*, $(C_9H_{10}N_4)_2,H_2PtCl_6$, crystallises from its hydrochloric acid solution in large, orange-coloured, monoclinic prisms melting and decomposing at 245° [$a:b:c = 3·21435 : 1 : 4·34494$; $\beta = 61°\ 40'$].

Dibenzoyl-3-*imido*-1 : 5-*diphenyltriazoline*, $C_2N_4Ph_2Bz_2$, obtained by heating phenylamidoguanidine hydrochloride and sodium benzoate, in molecular proportion, with excess of benzoic chloride, separates from alcohol in crystals melting at 194—195°, and it is neither acid nor basic in its properties. On hydrolysis, it yields 3-*imido*-1 : 5-*diphenyltriazol-ine*, $NPh{<}{{NH \cdot C\!:\!NH}\atop{CPh\!:\!N}}$, which crystallises from alcohol in monoclinic laminæ melting at 156° [$a:b:c = 0·88175 : 1 : 0·77171$; $\beta = 82°\ 6'$]. It dissolves very slightly in water, but is very soluble in alcohol, ether, or chloroform. It has no basic properties, being almost insoluble in dilute mineral acids, and forming neither a picrate nor a platinochloride. On boiling with an excess of acetic anhydride, it yields a *diacetyl* derivative, $C_2N_4Ph_2Ac_2$, which crystallises from light petroleum in stellate groups of lustrous needles melting at 119° ; it is soluble in alcohol, chloroform, benzene, or light petroleum, and on boiling with water, acetic acid is evolved and imidodiphenyltriazoline reproduced.

5 : 5-*Phenylene-bis*-3-*imido*-1-*phenyltriazoline*, $C_6H_4\!\left(C{\ll}{{NPh \cdot NH}\atop{N{-\!\!-}C\!:\!NH}}\right)_2$, is formed on heating corresponding quantities of phenylamidoguanidine hydrochloride and potassium phthalate with an excess of phthalic chloride ; it crystallises from alcohol in acicular plates melting at 261°, is almost insoluble in water or ether, but dissolves in alcohol or chloroform, and has basic properties, as it dissolves readily in mineral acids and is reprecipitated by potash.

5 : 5-*Ethylene-bis*-3-*imido*-1-*phenyltriazoline*, $C_2H_4\!\left(C{\ll}{{NPh \cdot NH}\atop{N{-\!\!-}C\!:\!NH}}\right)_2$, obtained when phenylamidoguanidine hydrochloride and potassium succinate, in molecular proportion, are heated with an excess of succinic chloride, is almost insoluble in water, chloroform, or benzene, and dissolves slightly in alcohol, from which it crystallises in needles melting at 390°. Its *picrate*, $C_{18}H_{18}N_8(C_6H_3N_3O_7)_2$, is moderately soluble in alcohol or chloroform, but only very slightly so in water, ether, or

benzene; it separates from alcohol in beautiful crystals melting and decomposing at 245°.

Phenylamidoguanidine hydrochloride and sodium carbonate, when heated with an excess of ethylic oxalate, do not give rise to bis-imidophenyltriazoline as might be expected, but to phenylimidotriazoline or, if the temperature is moderated, to oxalylphenylamidoguanidine. The latter forms a *picrate*, $C_2O_2[NPh\cdot NH\cdot C(NH)\cdot NH_2]_2, 2C_6H_3N_3O_7$, which is very soluble in alcohol, and separates from it in crystals melting at 174°.   T. H. P.

Action of Phosphorus Pentasulphide on Phenyl- and Paratolyl-urazole. By GUIDO PELLIZZARI and A. A. FERRO (*Gazzetta*, 1898, 28, ii, 541—563).—By the action of phosphorus pentasulphide on many oxygenated organic compounds, products of reduction are obtained as well as sulphur substitution derivatives. Thus Pellizzari and Cuneo (Abstr., 1895, i, 73) found that this reagent reduces urazole to triazole. The authors are of opinion that the oxygen atom is first displaced by sulphur, the reduction taking place subsequently, and they have succeeded in obtaining certain compounds intermediate between the sulphur derivatives and the products of reduction. With 1-phenylurazole, a mixture of three products is obtained by the action of phosphorus pentasulphide.

1-*Phenyl-3-thiotriazolone*, $NPh{<}^{CH:N}_{NH\cdot CS}$, separates from benzene in colourless, lustrous, acicular crystals melting at 189°; it is fairly soluble in alcohol, slightly so in ether, carbon bisulphide, or water, and insoluble in light petroleum; it acts both as an acid, yielding metallic derivatives with the alkali metals, and as a feeble base, forming an unstable hydrochloride. By treatment with phosphorus pentasulphide, it is converted into 3-thio-bis-1-phenyltriazole and 1-phenyltriazole, the former of which is also produced on heating it or on boiling its alcoholic solution. The *silver* derivative of phenylthiotriazolone, $C_8H_6N_3SAg$, is a white powder. The *barium* compound, $(C_8H_6N_3S)_2Ba$, crystallises in small needles. The authors have established the constitution given above by preparing the same compound synthetically from formic acid and phenylsemithiocarbazide.

3-*Thio-bis-1-phenyltriazole*, $S\left(C{<}^{N:CH}_{N\cdot NPh}\right)_2$, is only slightly soluble in any of the ordinary solvents except hot alcohol, from which it crystallises in long, shining, prismatic needles melting without decomposition at 136°; it is insoluble in potash even on heating, but dissolves in boiling hydrochloric acid, giving an unstable hydrochloride separating in white, acicular crystals. By the action of phosphorus pentasulphide, it yields the phenylthiotriazolone described above and 1-phenyltriazole.

By using paratolylurazole in place of the phenyl compound, the following paratolyltriazole derivatives were obtained:

1-*Paratolyl-3-thiotriazolone*, $C_7H_7\cdot N{<}^{CH:N}_{NH\cdot CS}$, is soluble in hot alcohol or benzene, and crystallises from the latter with half a mol. of benzene. It melts at 218°, sublimes unchanged at a slightly lower

temperature, and on further heating, gradually decomposes with the evolution of hydrogen sulphide and formation of thio-bis-tolyl-triazole. It dissolves in alkalis and gives white, curdy precipitates with silver nitrate and mercuric chloride, and a bluish-green precipitate with copper sulphate solution. The position of the sulphur atom was established by synthesising the compound from formic acid and *paratolylsemithiocarbazide*, $NH_2 \cdot CS \cdot NH \cdot NH \cdot C_7H_7$; this substance, prepared by the action of ammonium thiocyanate on paratolyl-hydrazine hydrochloride in alcoholic solution, is very soluble in alcohol, fairly so in benzene and ether, and forms shining, hexagonal laminæ melting at 150°. It is only slightly soluble in water, but dissolves readily in dilute solutions of alkalis or mineral acids. With silver nitrate and with yellow mercuric oxide, it gives black precipitates, and in the latter case imparts to the liquid a strong odour of bitter almonds.

3-*Thio-bis-1-paratolyltriazole*, $S\left(C{<}{\overset{N:CH}{\underset{N \cdot N \cdot C_7H_7}{|}}}\right)_2$, melts at 188°, crystallises from boiling alcohol in beautiful, yellowish needles, and is insoluble in the other ordinary solvents.

1-Paratolyltriazole was also obtained by the action of phosphorus pentasulphide on paratolylurazole.　　　　　　　　　T. H. P.

Hydromethylmorphimethine. By EDUARD VONGERICHTEN (*Ber.*, 1899, **32**, 1047—1050).—Methylmorphimethine is readily reduced by sodium in alcoholic solution to dihydromethylmorphimethine, whilst codeine, under the same conditions, remains unchanged; it therefore seems probable that the two additional hydrogen atoms in hydromethylmorphimethine are attached to two carbon atoms, between which a double linking has been produced by fission of the codeine ring.

Owing possibly to the conversion of the α-modification of methylmorphimethine into the β-modification of hydromethylmorphimethine on reduction, the latter substance is stable under conditions in which α-methylmorphimethine undergoes decomposition. Thus, on heating the hydro-base with acetic anhydride in a closed tube at 170° for 10—12 hours, it is only partially decomposed, and on treating the product with methylic iodide, the *methiodide*, $C_{20}H_{28}NO_4I$, crystallising from water in pale yellow needles and melting at 265°, is obtained. Further, on heating the methohydroxide of the hydro-base with acetic anhydride under the same conditions, only methylic alcohol is eliminated, and the monacetyl derivative is recovered unchanged.
　　　　　　　　　　　　　　　　　　　　　　　　J. F. T.

Solanine. By PAUL CAZENEUVE and P. BRETEAU (*Compt. rend.*, 1899, **128**, 887—890. Compare Abstr., 1879, 541).—The pulp obtained by grinding together potato seedlings and slaked lime is dried at the ordinary temperature and extracted with cold alcohol (93 per cent.); the alcoholic extract is distilled in a vacuum at 40—45°. The syrupy residue, on cooling, yields a crystalline mass, which is washed with ether and light petroleum, and repeatedly crystallised from alcohol. The product is solanine, and when obtained by this method it crystallises in colourless needles and melts at 250°. It is insoluble

in water and ether, dissolves slightly in cold alcohol, and is more soluble in the warm solvent. Analyses of a specimen dried at 105° gave numbers corresponding with those required for the formula $C_{28}H_{47}NO_{11}$; when crystallised from alcohol and dried at ordinary temperatures, the substance contains $2H_2O$. Although insoluble in water, the compound readily dissolves in dilute acids; this indicates a basic character, but it is scarcely alkaline to turmeric. On hydrolysis with hydrochloric acid, it is resolved into solanidine and a sugar possessing reducing properties and giving an osazone.

The solanine thus obtained differs from the preparations of earlier investigators in its behaviour towards concentrated mineral acids. With concentrated sulphuric and nitric acids, the base obtained by the authors slowly develops violet and pink colorations respectively; under these conditions, intense violet colorations were immediately produced from the older preparations. The authors' specimen remains colourless when treated with concentrated hydrochloric acid; the other preparations became yellow. Crystals of solanine develop a light green coloration when treated with warm alcoholic sulphuric acid, and the liquid in contact with the crystals acquires a pink tint; a solanine of German origin gave with this reagent a blood-red coloration.

<div align="right">G. T. M.</div>

Products of Oxidation of Cholic Acid. By LASSAR-COHN (*Ber.*, 1899, **32**, 683—687).—Cholic acid in alkaline solution kept saturated with carbonic anhydride, is oxidised to dehydrocholic acid by permanganate at the ordinary temperature; the yield is poor, however.

Bilianic acid, $C_{21}H_{31}O_2(COOH)_3$, is best obtained by dissolving cholic acid, freed from alcohol, in aqueous sodium carbonate, pouring the solution into 2 per cent. potassium permanganate, decolorising after two days with sodium hydrogen sulphite and sulphuric acid, and filtering after a further twenty-four hours; the yield is 53 per cent. The crude product contains about 2 per cent. of isobilianic acid; to remove this, it is treated with boiling baryta water; barium isobilianate is insoluble, the bilianate soluble, in hot water. The acids are recrystallised by dissolving them in a little alcohol and diluting the solution with water.

Cilianic acid, $C_{17}H_{25}O_3(COOH)_3 + H_2O$, is obtained by dissolving bilianic acid in 12 per cent. caustic soda, adding a dilute solution of potassium permanganate, and boiling vigorously in a flask for twenty minutes or so, until decolorisation is complete. The product of ten such operations was mixed with sodium hydrogen sulphite, and 20 per cent. sulphuric acid, until it was decolorised and acid in reaction; from this solution, the cilianic acid separated in the course of twenty-four hours; it was recrystallised from alcohol and water. It melts at 242°, forms a silver salt of apparently abnormal composition, and has about half the normal molecular weight in freezing acetic acid and boiling ethereal solution; this is perhaps due to the fact that it contains $1H_2O$ which cannot be removed by drying, but is possibly split off in solution. The *trimethylic* salt, prepared from the silver salt and methylic iodide, melts at 119°, and has the normal molecular weight in freezing phenol solution.

<div align="right">C. F. B.</div>

Organic Chemistry.

Alkyl, Alphyl, and Arryl. By DANIEL VORLÄNDER (*J. pr. Chem.*, 1899, [ii], 59, 247).—The author recommends the use of the term alkyl for all univalent hydrocarbon radicles, dividing them further into alphyl or fatty, such as CH_3, C_2H_5, &c.; arryl or aromatic, such as C_6H_5; and alpharryl, aromatic radicles with fatty characters, such as benzyl, nitrobenzyl, &c. He proposes the term acyl as a general term for all acid radicles. F. H. N.

Action of Nitric Acid and of Nitrosulphuric Acid on Saturated Hydrocarbons. By WLADIMIR B. MARKOWNIKOFF (*Ber.*, 1899, 32, 1441—1445. Compare Francis and Young, Trans., 1898, 73, 928).—All paraffins of the types $CHR_2 \cdot CHR_2$ and CHR_3 (where $R = CH_3$ or any normal alkylic group) are readily acted on by nitric acid of sp. gr. 1·535; oxidation takes place slowly at 0°, but at a slightly higher temperature the reaction is very violent, the chief products being acetic acid and carbonic anhydride together with small quantities of oxalic acid; succinic acid is also formed when small quantities of naphthenes are present. Di-isobutyl, in addition, yields isobutyric acid, and di-isoamyl, a higher fatty acid. Crystalline tertiary nitro-derivatives are also formed, only one of which, *trinitrodimethyl-propylmethane*, $NO_2 \cdot CMe_2 \cdot C(NO_2)_2 \cdot CH_2Me$, crystallising in needles and melting at 95°, has been analysed. Di-isobutyl yields a small quantity of a nitro-derivative melting at 87—88°, probably identical with Francis and Young's trinitrodi-isobutyl melting at 91°. The stability of normal paraffins towards concentrated nitric acid at ordinary temperatures has been confirmed.

Trimethylethylmethane (see following abstract), as a type of the hydrocarbons CR_4, is only slowly acted on by nitric acid at the ordinary temperature; it is, however, more readily attacked than normal hexane.

Nitrosulphuric acid, which the author regards as a solution of $OH \cdot SO_2 \cdot O \cdot NO_2$ in sulphuric acid, acts quite differently from concentrated nitric acid; a few degrees above 0°, it has practically no action on tertiary hydrocarbons, and the hydrocarbons of lower boiling point may even be distilled over nitrosulphuric acid without undergoing any great decomposition; with aromatic hydrocarbons, nitrosulphuric acid behaves as a stronger oxidising agent than nitric acid itself. Of the naphthenes, hexanaphthene is less readily acted on than its homologues, being quite as stable as normal hexane; penta- and hepta-methylene behave similarly, being oxidised only when heated with the acid and then quite regularly, a dibasic acid containing the same number of carbon atoms as the original hydrocarbon being formed. Methyl- and dimethyl-pentamethylenes, and methyl- and dimethyl-hexanaphthenes are readily attacked by concentrated nitric acid, yielding dibasic acids. The action of nitrosulphuric acid on these cyclic hydrocarbons and on the paraffins is similar. J. J. S.

Quaternary Paraffins, CR₄. By WLADIMIR B. MARKOWNIKOFF (*Ber.*, 1899, **32**, 1445—1449).—Trimethylethylmethane occurs in Caucasian naphtha, and is best obtained in a pure form from this source by nitrating the fraction of naphtha boiling at 50—51° three times at 100° with nitric acid of sp. gr. 1·235, and then boiling with acid of sp. gr. 1·4. It is also probably contained in American petroleum. It was proved to be identical with Goriaïnoff's synthetical hydrocarbon (*Annalen*, 1874, **165**, 107), which, however, boils at 49·6—49·7° under 760 mm. pressure, and not, as he stated, at 43—48°; it has a sp. gr. 0·6662 at 0°/0° and 0·6488 at 20°/0°. Further proof of its constitution is given by the fact that its nitro-derivative, when reduced by alkaline stannous chloride, yields an oxime which, on hydrolysis, gives a mixture of ketones from which pinacoline can be isolated. The *nitro*-derivative, $CMe_3 \cdot CHMe \cdot NO_2$, is crystalline, melts at 40°, distils at 167·5—167·8° under 748 mm. pressure, has an odour of camphor, sublimes readily, and is soluble in alcohol, and especially in light petroleum; no trace of a primary nitro-compound is formed when the hydrocarbon is nitrated. When reduced with tin and hydrochloric acid, the *amine*, $CMe_3 \cdot CHMe \cdot NH_2$, boiling at 101·5—102·5° is obtained; its *hydrochloride* crystallises in small needles, does not melt below 245°, and is readily soluble in water; the *platinochloride* crystallises in four-sided, orange-coloured prisms or glistening cubes, and is readily soluble in water or alcohol; the *aurichloride*, $C_6H_{13} \cdot NH_2, HAuCl_4$, is less soluble, and crystallises in needles melting at 186—187° and decomposing at 196°. The same base may be obtained by the reduction of *pinacolinoxime*, which crystallises from light petroleum in large plates melting at 77—78° and boiling at 171·6° under 748 mm. pressure.

Tetramethylmethane is probably contained in the gases from Caucasian naphtha. J. J. S.

Theory of Unsaturated and of Aromatic Compounds. By JOHANNES THIELE (*Annalen*, 1899, **306**, 87—142).—The author holds the view that, in unsaturated compounds, whilst two affinities of every atom which participates in the double linking are occupied with those of the contiguous atom, the combining energy is not completely absorbed, so that the atoms in question still possess valency (*Partialvalenz*), and it is in this partial valency that the source of additive capacity is to be found. The idea may be expressed by the symbols, ····C꞊C····, ····C꞊O····, &c.

It is pointed out that the system C꞊C—C꞊C takes up hydrogen or bromine at the extremities, becoming CH—C꞊C—CH or CBr—C꞊C—CBr. The central carbon atoms appear to have lost their additive function, which is inconsistent with the scheme ····C꞊C—C꞊C····; in other words, each has lost its partial valency, which is engaged in balancing that of the other, according to the symbol ····C꞊C꞊C꞊C····. A new form of double linking has been thus produced having no partial valency; it is therefore suitably termed inactive (*inactive*). The author refers to systems typified by the foregoing, as conjugated (*conjugirt*).

If the extremities of a conjugated system exert their additive capabilities, the central carbon atoms become active, and their partial valency reappears, as indicated by the symbol $CH—C \rlap{\vdots}{=} C—CH$.

These principles are applicable to a very large number of chemical changes, but it is not possible to do justice to the discussion in an abstract. M. O. F.

Oxidation of Unsaturated Compounds with Potassium Permanganate. By IWAN L. KONDAKOFF (*J. pr. Chem.*, 1899, [ii], 59, 287—292).—According to Wagner (Abstr., 1890, 1313; 1892, 310, &c.), when unsaturated compounds are oxidised with permanganate, the first action consists in the addition of hydroxyl groups, the number added being equal to that of the atoms of bromine with which the substance is able to combine, the resulting glycol subsequently undergoing further oxidation; he maintains, moreover, that, during the oxidation, neither hydration nor dehydration takes place. Saytzeff (Abstr., 1886, 140) and others have shown, however, that an oxide is probably the first product, and that subsequent hydration may account for the production of a glycol.

The author discusses the question in detail, with special reference to the production of oxoctenol from dimethyltertiarybutylethylene (Butleroff, Abstr., 1878, 121; 1882, 936) and the formation of ecgonine during the oxidation of anhydroecgonine. He holds that oxygen is added first and that then hydration takes place. A. L.

Hydrogenation of Acetylene in Presence of Nickel. By PAUL SABATIER and JEAN BAPTISTE SENDERENS (*Compt. rend.*, 1899, 128, 1173—1176).—When mixtures of acetylene and hydrogen are passed over finely divided, reduced nickel at the ordinary temperature, interaction takes place and heat is developed, so that the temperature of the metal gradually rises. The chief reaction is the formation of ethane, but the composition of the crude product depends on the relative proportions of acetylene and hydrogen, the temperature, and the velocity of the gaseous current. Ethylene is formed in considerable quantity, together with liquid products consisting chiefly of paraffins with some olefines, and a small quantity of benzene. The proportion of liquid products is greater the higher the temperature and the lower the proportion of hydrogen present. As the proportion of acetylene in the original gaseous mixture is increased, the proportion of benzene hydrocarbons in the product also increases until eventually the metal intumesces and becomes incandescent, as Moissan and Moureu observed with pure acetylene and nickel (Abstr., 1898, i, 585).

The nickel undergoes no change, except that a small quantity of carbon is deposited on it.

Iron, cobalt, and copper behave similarly, and these facts may throw light on the origin of petroleum. C. H. B.

Action of Bromine on $\alpha\beta$-Propylenic Bromide in Presence of Anhydrous Aluminium Bromide: Preparation of $\alpha\alpha\beta$-Tribromopropane. By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, [iii], 19, 805—807).—A solution of aluminium bromide in bromine was gradually added to a mixture of $\alpha\beta$-propylenic bromide with bromine,

maintained at about 25°, and the product subsequently thrown into cold, dilute hydrobromic acid. The oily liquid which separated, on fractional distillation under diminished pressure, gave (1) 65—70 per cent. of the theoretical yield of a substance which, by analysis and by its conversion into monobromopropylene, $CHMe:CHBr$, when treated with zinc powder in alcoholic solution, was proved to be $\alpha\alpha\beta$-tribromopropane, $CHMeBr \cdot CHBr_2$; (2) a small quantity, never exceeding 7—8 per cent., of a liquid having the composition of a tribromopropane, which yields triacetin when heated with silver acetate at 110°, and is, therefore, regarded as tribromhydrin, $H_2Br \cdot CHBr \cdot CH_2Br$; (3) a very small quantity of $\alpha\alpha\beta\gamma$-tetrabromopropane (see following abstract). N. L.

Action of Bromine on $\alpha\alpha\beta$-Tribromopropane and on Tribromhydrin in Presence of Aluminium Bromide: Preparation of $\alpha\alpha\beta\gamma$-Tetrabromopropane. By A. MOUNEYRAT (Bull. Soc. Chim., 1898, [iii], 19, 807—810).—A solution of aluminium bromide in bromine was gradually added to a mixture of $\alpha\alpha\beta$-tribromopropane with bromine maintained at a temperature of about 50°. The product, when fractionally distilled, yielded 60—65 per cent. of a heavy liquid boiling at 138—140° under 17 mm. pressure and having the composition of a tetrabromopropane, together with a smaller quantity of a heavy liquid boiling at 165—175° under 17 mm. pressure, which proved to be a pentabromopropane. The tetrabromopropane thus obtained has in all probability the constitution represented by the formula $CH_2Br \cdot CHBr \cdot CHBr_2$, since it is identical with the product of the action of bromine on β-epidibromhydrin, $CH_2Br \cdot CH:CHBr$, and also with the tetrabromopropane formed by the bromination of tribromhydrin, $CH_2Br \cdot CHBr \cdot CH_2Br$, in presence of aluminium bromide. It becomes viscous, but does not crystallise, when cooled to the boiling point of methylic chloride, and is converted by heating with an alcoholic solution of potassium acetate into a tribromopropane boiling at 210—220°, which reacts with bromine in sunlight to form a liquid pentabromopropane.

The pentabromopropane which, as stated above, is formed by the action of bromine on tribromopropane, is more readily obtained by brominating $\alpha\alpha\beta\gamma$-tetrabromopropane. It was not prepared in sufficient quantity to allow of its constitution being definitely established, but as the central carbon atom in the halogen derivatives of propane is brominated with most difficulty, it probably has the formula $CHBr_2 \cdot CHBr \cdot CHBr_2$. N. L.

Behaviour of Tetramethylethylenic Dibromide towards Alcoholic Potash. By IWAN L. KONDAKOFF (J. pr. Chem., 1899, [ii], 59, 293—301).—The author has repeated Couturier's work on the action of alcoholic potash on tetramethylethylenic dibromide. The product has an odour of allene and of ethylic valerate, and so far from being a pure substance, as stated by Couturier, is divisible into four fractions; about two-thirds boils at 69—74°, a very small quantity at 74—130°, a small quantity at 130—140°, and the portion of higher boiling point sets to a mass of needles.

The fraction 69—74° has a sp. gr. 0·7350 at 0°, and 0·7077 at 18°,

and a molecular refractive power 29·32 for sodium light. (Calculated for C_6H_{12} with one ethylenic union $[M]_D = 29·4$). It absorbs bromine in ethereal solution at $-10°$, yielding a mixture of crystalline substances, and also forms compounds with hydrogen chloride. The crystalline residue, which at first melted at 152°, appeared to be a mixture of at least two substances.

It is concluded that Couturier's product is a mixture of at least two hydrocarbons, namely, tetramethylethylene, and either di-isopropenyl or a cyclic hydrocarbon. The author finally gives his view of the nature of the changes which take place during the production of the mixture.   A. L.

Action of Cuprous Chloride on Nitriles. By CH. RABAUT (*Bull. Soc. Chim.*, 1898, **19**, [iii], 785—788).—Cuprous chloride and the nitriles do not react in the presence of ammonia, but combination takes place in cold hydrochloric acid solutions. The substances produced are insoluble in water or the neutral solvents, and form colourless crystals which readily oxidise on exposure to air. Hydrogen cyanide is completely absorbed by a saturated solution of the chloride in hydrochloric acid; the resulting *compound* has the composition $HCN,Cu_2Cl_2,2HCl$. Acetonitrile similarly treated yields the *compound* $2CH_3 \cdot CN,Cu_2Cl_2$. Propionitrile and its higher homologues are more or less hydrolysed by this reagent, and do not yield compounds of this type. The substance $C_2N_2,2Cu_2Cl_2$ is obtained from cyanogen, whilst succinonitrile gives rise to $2CH_4(CN)_2,Cu_2Cl_2$. Benzonitrile and phenylacetonitrile yield $2CNPh,Cu_2Cl_2$ and $4C_6H_5 \cdot CH_2 \cdot CN,Cu_2Cl_2$ respectively. The *substance* $C_6H_4Me \cdot CN,Cu_2Cl_2$ is obtained from orthotoluonitrile, and the para-compound gives $2C_6H_4Me \cdot CN,Cu_2Cl_2$, but the meta-isomeride does not react with cuprous chloride. 2 : 4 -Dimethylbenzonitrile produces the *compound,* $2C_6H_3Me_2CN,Cu_2Cl_2$. α- and β-Naphthonitriles yield white, crystalline compounds, $2C_{10}H_7 \cdot CN,Cu_2Cl_2$. Substituted nitriles do not react with cuprous chloride, and negative results were obtained with the following compounds : cyanacetic acid, glycollonitrile, propionylpropionitrile, amygdalin, and the para- chloro-, bromo-, and nitro-derivatives of benzonitrile. These additive products may also be obtained by warming dry cuprous chloride with the nitrile ; should the latter be a solid, combination may be effected in alcoholic solution. This property of the nitriles may be employed in their isolation and purification : a solution containing a nitrile is treated with a cold saturated hydrochloric acid solution of cuprous chloride, and the precipitate collected and washed with alcohol ; the nitrile is regenerated from the additive product by decomposing the latter with either ferric chloride or hydrogen sulphide, and extracted by means of an appropriate solvent ; the former method of decomposition seems to give the better results.   G. T. M.

Formation of Potassium β-Ferricyanide through the Action of Acids on the Normal Ferricyanide. By JAMES LOCKE and GASTON H. EDWARDS (*Amer. Chem. J.*, 1899, **21**, 413—418. Compare Abstr., 1899, i, 407).—The use of an oxidising agent in the preparation of potassium β-ferricyanide from the normal ferricyanide is found to be unnecessary ; the change is due to the hydrochloric acid used,

and may be effected by the use of small quantities of mineral acids. Even feeble acids, such as oxalic or acetic acids, are capable of inducing the transformation ; the velocity of the change, however, diminishes with decrease in ionisation of the acid used.   A. L.

Cyanuric Compounds.—By OTTO DIELS (*Ber.*, 1899, **32**, 1219—1220).—The compound previously described as diamidocyanuric hydride (compare this vol., i, 406) is identical with Nencki's formoguanamine (this Journal, 1875, 754). The substance melts, however, at 329° (corr.), although it is stated by Nencki not to melt below 350°. The formation of formoguanamine from cyanuric chloride affords a further proof of the constitution of the former compound (Weith, *Ber.*, 1876, **9**, 460).   A. H.

Methylic Phosphates. By JACQUES CAVALIER (*Bull. Soc. Chim.*, 1898, [iii], **19**, 883—887).—Monomethylic and dimethylic phosphates are readily obtained by the action of phosphoric anhydride on methylic alcohol in ethereal solution, the two acids being separated by conversion into their barium salts, which differ greatly in solubility. If the quantity of phosphoric anhydride employed is rather less than that corresponding with the formation of the dimethylic phosphate, a yield of about 65 per cent. of monomethylic and 30 per cent. of dimethylic phosphate is obtained.

Barium methylic phosphate, $PO_4MeBa + H_2O$, crystallises in white scales which become anhydrous at 100°, and are less soluble in hot than in cold water, one hundred grams of the solution containing 1·83 grams of the anhydrous salt at 15°, 1·42 grams at 40°, and 0·62 gram at 70°. Like the analogous ethylic and allylic derivatives, monomethylic phosphate is rendered neutral to methyl-orange by addition of 1 mol. of alkali, whereas if phenolphthalein is employed as the indicator, the neutral point is only reached when 2 mols. of alkali have been added. By taking advantage of these facts, a number of acid salts of the general formula PO_4MeMH have been prepared ; these are all neutral to methyl-orange, but acid to phenolphthalein. The *barium* salt, $(PO_4MeH)_2Ba + H_2O$, is much more soluble in water than the normal salt described above, one hundred grams of the solution containing 23·1 grams of the anhydrous salt at 15°, 24·0 grams at 36°, 24·7 grams at 60°, 26·5 grams at 73°, and 28·6 grams at 85°. The *strontium* salt crystallises, like the barium salt, with $1H_2O$, whereas the calcium salt is anhydrous, as also are the *potassium*, *ammonium*, and *sodium* salts. These are all soluble, crystalline compounds which lose methylic alcohol on ignition, and leave a residue of metaphosphate.

Barium dimethylic phosphate, $(PO_4Me_2)_2Ba$, is obtained in the preparation of the methylic phosphates as an indefinitely crystalline mass very soluble in water. The *lead* salt forms colourless, slender needles, which are more soluble in hot than in cold water, melt at 155°, and decompose at about 225° with the production of trimethylic phosphate. Dimethylic hydrogen phosphate is most conveniently prepared by decomposing the lead salt with hydrogen sulphide.   N. L.

Preparation of Mixed Ethers. By ARNOLD H. PETER (*Ber.*, 1899, **32**, 1418—1421).—When a mixture of amylic alcohol (boiling

at 132—133°) and ethylic alcohol is mixed with an equal weight of 85 per cent. sulphuric acid, and the temperature of the whole maintained at 135—140° while more of the alcoholic mixture is run in, but little sulphurous anhydride is evolved, and the distillate, when washed and distilled twice over solid caustic potash, boils at 40—180°. On fractionation, a considerable portion boils at 79—81°; this undoubtedly contains ethylic alcohol, but the greater part of it does not dissolve in water, and is found to be ethylic amylic ether, boiling at 112° and of sp. gr. 0·761 at 18°. The fraction which boils at 81—130° contains ethylic amylic ether, amylic alcohol, and diamylic ether; on the small scale, the alcohol is best removed by treatment with 85 per cent. sulphuric acid, after which the ethers may be separated by fractional distillation.

These results confirm those of Williamson (*Annalen*, 1851, 77, 37; 1852, 81, 73). Guthrie (*ibid.*, 1858, 105, 37) and Norton and Prescott (Abstr., 1885, 496) have doubted the possibility of obtaining ethylic amylic and methylic amylic ethers by the process in question; they probably used acid of too great strength.　　　　C. F. B.

Dextrins of Saccharification. By PAUL PETIT (*Compt. rend.*, 1899, 128, 1176—1178).—The action of amylase on starch at 70° yields a dextrin, $(C_6H_{10}O_5)_3$, with a rotatory power $a_D = 166·6$ and a reducing power equivalent to 18 per cent. of maltose. Prolonged action of the amylase partially converts it into maltose. With barium hydroxide, it yields the compound $2C_6H_{10}O_5,C_6H_8O_5Ba$. The action of amylase on various worts yields dextrins which form barium compounds corresponding with the molecular formulæ $(C_6H_{10}O_5)_2$, $(C_6H_{10}O_5)_4$, and $(C_6H_{10}O_5)_5$. *Penicillium glaucum* and *Aspergillus niger* in active growth, and the liquid pressed out from yeast, also have the property of partially converting dextrin into maltose.
　　　　　　　　　　　　　　　　　　　　　　　　　　C. H. B.

Nitrocellulose. By GEORG LUNGE and E. WEINTRAUB (*Zeit. angew. Chem.*, 1899, 441—448, 467—475).—By the action of concentrated nitric acid on a solution of cellulose in concentrated sulphuric acid, a substance is obtained which is soluble in acetone, ethylic acetate, methylic and ethylic alcohols, and in concentrated nitric acid. This compound contains nitrogen corresponding in amount with that required for a pentanitrocellulose, and is possibly a pentanitrocellulose-dextrin or a pentanitramyloid. By increasing the proportion of sulphuric acid to nitric acid in the ordinary process of nitration, the velocity of the reaction is very greatly decreased, and the product contains less nitrogen; when the ratio of the sulphuric acid to the nitric acid is 8 to 1 or more, some of the cellulose is not attacked. Nitration takes place much more rapidly at higher temperatures, but there is a greater loss of material by solution in the acid; the nitrocellulose obtained by nitrating at 40° contains less nitrogen than that prepared at the ordinary temperature. The presence of nitric peroxide in the nitric acid used for nitration has apparently little or no effect until its amount reaches 12 per cent., when the degree of nitration effected is slightly diminished. The highest nitrated products, when examined under the microscope in polarised light, have a characteristic light or

dark blue appearance, but it is impossible to distinguish hexanitrocellulose from pentanitrocellulose. As the percentage of nitrogen decreases, the blue gradually fades into grey. The presence of cellulose in the product is easily detected by the brilliant yellow to reddish coloration, but the intensity of the coloration does not afford a trustworthy indication of the quantity present. To determine the amount of free cellulose, about 5 grams of the nitrocellulose are heated at 40—50° for 20—30 minutes with 150 c.c. of a mixture of 100 c.c. of acetone with 100 c.c. of ordinary alcohol in which 2—3 grams of sodium have been dissolved. The nitrocellulose is destroyed by sodium methoxide or ethoxide, and also, but more slowly, by sodium amyloxide. The brown, insoluble residue is washed with alcohol and water by decantation, collected, and finally washed with hot water containing a little hydrochloric acid; it still contains traces of nitrocellulose, which may be removed by repeating the process. The cellulose obtained is colourless when wet, but very slightly yellow when dry; the colour may be removed by means of bleaching powder.

E. W. W.

Oxycellulose Osazones. By Léo Vignon (*Compt. rend.*, 1899, **128**, 1038—1040).—Phenylhydrazine combines with oxycellulose in presence of acetic acid, but the quantity which enters into combination varies with the nature of the oxycellulose, and is higher the more completely the cellulose has been oxidised. The action of potassium chlorate and hydrochloric acid, or of chromic acid and dilute sulphuric acid for not too long a time, gives the best results, and the product combines with about 8 per cent. of phenylhydrazine. The tendency of the oxycelluloses to combine with phenylhydrazine varies in the same order as their tendency to yield furfuraldehyde (Abstr., 1898, i, 620).

The osazones most probably have the constitution

$$\begin{matrix} NHPh \cdot N{:}CH \\ NHPh \cdot N \end{matrix}{>}C \cdot CH(OH) \cdot CH(OH) \cdot CH{<}\begin{matrix} CO \\ | \\ O \end{matrix}.$$
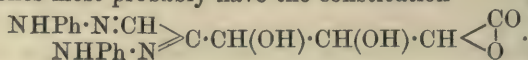
C. H. B.

The So-called Lignin Reaction of Wood. By Friedrich Czapek (*Zeit. physiol. Chem.*, 1899, **27**, 141—166).—An historical survey of the more important researches on the constituents and colour reactions of woody tissues. A substance termed *hadromal* has been isolated from different woody tissues; it has the properties of a phenol and of an aldehyde, is probably a para-compound, and is regarded as the active principle which causes the more characteristic colorations of woody tissues. Minute quantities of this principle appear to be extracted when finely-divided wood is treated with boiling benzene, alcohol, or ether, since the solutions thus obtained give the same colour reactions as the wood itself. A somewhat larger quantity is obtained when the woody tissue is first heated with stannous chloride for about three hours and then extracted with benzene. It is best purified by solution in light petroleum, conversion into its sodium hydrogen sulphite compound, and finally by several recrystallisations from light petroleum, when it is obtained as a pale yellowish-brown, crystalline powder which gives the lignin reactions of wood in a marked degree. The

compound has not been obtained quite pure, and has not been analysed. It has an aromatic odour, sinters at 50—60°, and melts at 75—80°. It does not contain nitrogen, is sparingly soluble in hot water, readily in alcohol and most organic solvents, also in alkalis; it is not volatile with steam, and has the properties of an aldehyde and also of a phenol. Its benzoyl derivative and phenylhydrazone have been prepared, but not examined. The amount present is not more than 1—2 per cent. of the dry woody tissue, and it is thought that although a part of the compound exists in the free state, the greater part is in combination as a hadromal-cellulose, which becomes decomposed by the stannous chloride. J. J. S.

Action of Nitrosyl Chloride on Fatty Amines. III. Primary Diamines. By WASSILY A. SOLONINA (*Chem. Centr.*, 1899, i, 25—27; from *J. Russ. Chem. Soc.*, 1898, **30**, 606—632. Compare this vol., i, 473).—By mixing cooled solutions of nitrosyl chloride and ethylenediamine in metaxylene, nitrogen is evolved and a white precipitate of salts formed. After treating with water, the dry metaxylene solution yields ethylenic chloride, which, by the action of sodium phenoxide, forms diphenoxyethane, $C_2H_4(OPh)_2$, melting at 97—98°.

When ethereal solutions of nitrosyl chloride and hexamethylene-diamine, $C_2H_4(CH_2 \cdot NH_2)_2$, are mixed at 0°, nitrogen is liberated and a white precipitate formed. By treating the product with water, removing the ether, distilling first with steam and then under reduced pressure, a fraction boiling at 200—205° or at 85—105° under 25—30 mm. pressure is obtained. It has the composition of a hexylenic chloride, $C_6H_{12}Cl_2$, but contains two isomerides and a small quantity of an unsaturated compound. When treated with sodium phenoxide and distilled with steam, *phenoxyhexylene*,

$$CHMe{:}CH \cdot [CH_2]_2 \cdot CH_2 \cdot OPh,$$
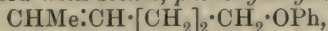
formed mainly from the hexylenic chloride, is obtained; this substance may also be prepared by the action of sodium phenoxide on methylpentamethylene bromide, $CHMeBr \cdot [CH_2]_3 \cdot CH_2Br$, and boils at 200—205°. The residue from the distillation in steam, when treated with potassium hydroxide and extracted with ether, yields 1:5-*diphenoxy-hexane*, $OPh \cdot CHMe \cdot [CH_2]_3 \cdot CH_2 \cdot OPh$, as an oil, and 1:6-*diphenoxyhexane*, $OPh \cdot CH_2 \cdot [CH_2]_4 \cdot CH_2 \cdot OPh$. The former indicates the production of methylpentamethylene chloride in the original reaction. The latter crystallises in monoclinic prisms (Popoff), melts at 82·5°, dissolves sparingly in cold water but easily in hot alcohol, benzene or ether; when treated with hydrochloric acid at 165—175°, it forms hexamethyl-enic chloride boiling at 203—205°, hence this compound is probably a product of the original reaction. An unsaturated chloro-compound, probably $CHMe{:}CH \cdot CH_2 \cdot CH_2 \cdot CH_2Cl$, is also obtained.

By the action of nitrosyl chloride on heptamethylenediamine, compounds similar to those obtained in the case of hexamethylene-diamine are formed, but only *heptamethylenic chloride*, $C_5H_{10}(CH_2Cl)_2$, was identified by means of the diphenoxy-derivative, which melts at 54·5—55°, is easily soluble in benzene and alcohol, and when heated with hydrobromic acid at 160—170°, yields heptamethylenic bromide.

By the action of nitrosyl chloride on octomethylenediamine, a distillate boiling at 132—138° under 20—25 mm. pressure is obtained; it contains several compounds, for by the action of sodium phenoxide it yields an *unsaturated monophenoxy*-derivative together with a liquid and a solid crystalline *diphenoxyoctane*, $C_8H_{16}(OPh)_2$. The unsaturated compound is easily volatile in steam, boils at 282—286°, combines with bromine, does not form an insoluble, amorphous compound with sulphurous anhydride, and has probably therefore the constitution $CHMe:CH\cdot[CH_2]_4\cdot CH_2\cdot OPh$; hence a chloride,

$$CHMeCl\cdot[CH_2]_5\cdot CH_2Cl,$$
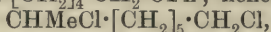
is possibly formed in the original reaction. The liquid diphenoxy-derivative is probably 1 : 7-*diphenoxyoctane*, is not volatile in steam, boils at 240—250° under 20—25 mm. pressure, and is probably formed from methylheptamethylenic chloride, $CHMeCl\cdot[CH_2]_5\cdot CH_2Cl$. The crystalline diphenoxyoctane, derived from octomethylenic chloride in the original product, crystallises in small plates, is not volatile in steam, melts at 83·5—84°, and is easily soluble in hot alcohol and in ether or benzene; it combines with hydrogen bromide to form the bromide, $CH_2Br\cdot[CH_2]_6\cdot CH_2Br$, which melts at 15—16°, boils at 150—161° under 20—25 mm. and at 270—272° under the ordinary pressure, with slight decomposition. The corresponding chloride boils at 240—242°.

By the action of nitrosyl chloride on nonomethylenediamine, compounds similar to those obtained in the preceding cases are formed. The products of the reaction, when treated with sodium phenoxide, give (1) an unsaturated phenoxy-derivative, probably

$$CHMe:CH\cdot[CH_2]_5\cdot CH_2\cdot OPh,$$
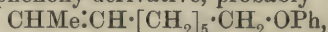
which combines with bromine, is volatile in steam, and dissolves easily in alcohol, ether, or benzene, and (2) *diphenoxynonane*,

$$OPh\cdot CH_2\cdot[CH_2]_7\cdot CH_2\cdot OPh,$$
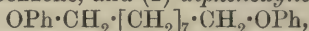
which crystallises in white leaflets, melts at 62°, is not volatile in steam, is soluble in hot alcohol, ether, or benzene, and combines with hydrogen bromide to form nonomethylenic bromide boiling at 285—288°, with liberation of hydrogen bromide, and at 171—173° under 20—25 mm. pressure. By the action of hydrochloric acid on diphenoxynonane, *nonomethylenic chloride* is formed; it is a colourless liquid, boils at 258—262° with partial decomposition, and is easily volatile in steam.

The action of nitrosyl chloride on diamines is similar to that on monamines, nitrogen being liberated and dichloro-derivatives formed, possibly by means of the intermediate production of tetrazo-compounds. The formation of isomerides and of unsaturated compounds, however, is much more marked than in the case of monamines, and nitroso-compounds are probably also produced.

This reaction affords a method of preparing dihalogen derivatives from diamines, for although the yield is poor, it compares favourably with the methods of Geuther, Simonini, &c.   E. W. W.

Stereochemistry of Nitrogen Compounds. By CARL D. HARRIES and TAMEMASA HAGA (*Ber.*, 1899, **32**, 1191—1199. Compare Abstr., 1898, i, 293).—When the hydrochloride of either of the stereoisomeric

2 : 4-diaminopentanes is heated with fused sodium acetate, it yields an *ethenyl* derivative, $CH_2 \begin{smallmatrix} CHMe \cdot NH \\ CHMe \cdots N \end{smallmatrix} CMe$. That from the labile α-base crystallises in thin plates, melts at 73°, is very hygroscopic, has a strongly alkaline reaction, absorbs carbonic anhydride from the air, and forms a crystalline *nitrate* melting at 194°, a *sulphate*, and a *hydrochloride*. That from the stable β-base is similar in properties, but melts at 102°, whilst the nitrate melts at 250°. On boiling α-diaminopentane with sodium and alcohol, it is converted into the β-base.

T. M. L.

Synthesis of Glycocine. By PAUL BOURCET (*Bull. Soc. Chim.*, 1898, [iii], **19**, 1005—1006).—Harting (*J. pr. Chem.*, **46**, 1) has shown that ethylic chloracetate interacts with hexamethylenamine forming a compound of the formula $CO \begin{smallmatrix} CH \cdot C_6H_{12}N_4Cl \\ C_6H_{12}N_4 \end{smallmatrix}$, and it is now found that a good yield of glycocine is obtained when this substance is heated with a mixture of alcohol and hydrochloric acid according to the general method for the preparation of amines suggested by Delépine (Abstr., 1897, i, 394).

N. L.

Chrysean. By GUSTAF HELLSING (*Ber.*, 1899, **32**, 1497—1498). —Chrysean, which has been prepared by Wallach (this Journal, 1874, 1086) by passing hydrogen sulphide into a saturated solution of potassium cyanide, may be obtained by the action of concentrated potassium cyanide on thioformamide (Hofmann, Abstr., 1878, 396). From this method of formation, the author deduces the constitution $NH[CH(CN) \cdot SH]_2$ for the substance.

J. J. S.

Chlorophosphines of the Aliphatic Series. By FR. GUICHARD (*Ber.*, 1899, **32**, 1572—1581).—Monalkyldichlorophosphines of the type $R \cdot PCl_2$ are best prepared by heating together a mixture of the mercuryalkyl and phosphorus trichloride in a sealed tube for 6 hours at 250°, at which temperature the alkyl mercurichloride which is formed in the reaction, and which not only makes the product difficult to purify but is dangerous to health, is entirely decomposed into calomel and the hydrocarbon. The monalkyldichlorophosphines are clear, mobile liquids of sharp, unpleasant odour, which are decomposed by water, and in the presence of moisture are coloured yellow.

Ethylchlorophosphine, $PEtCl_2$, boils at 114—117°, and has a sp. gr. 1·2952 at 19°.

Propylchlorophosphine, PPr^aCl_2, boils at 140—143°, and has a sp. gr 1·1771 at 19°.

Isopropylchlorophosphine, $PPr^\beta Cl_2$, boils at 135—138°, and has a sp. gr. 1·2181 at 23°.

Isobutylchlorophosphine, $C_4H_9 \cdot PCl_2$, boils at 155—157°, and has a sp. gr. 1·1236 at 23°.

Isoamylchlorophosphine, $C_5H_{11} \cdot PCl_2$, boils at 180—183°, and has a sp. gr. 1·1024 at 23°.

Monalkylphosphinous acids of the type $R \cdot PO_2H_2$ are prepared from the chlorophosphines by decomposition with water; they are

colourless syrups which solidify below 0°, and are moderately soluble in water; they are monobasic, and evidently have the structural formula $O:PHR'\cdot OH$.

Ethylphosphinous acid, PO_2H_2Et, has a sp. gr. 1·2952 at 19°.

Propylphosphinous acid, $PO_2H_2Pr^a$, has a sp. gr. 1·1418 at 13°.

Isopropylphosphinic acid, $PO_2H_2Pr^\beta$, has a sp. gr. 1·1891 at 19°.

Isobutylphosphinic acid, $C_4H_9\cdot PO_2H_2$, has a sp. gr. 1·0740 at 23°.

Isoamylphosphinic acid, $C_5H_{11}\cdot PO_2H_2$, has a sp. gr. 1·0613 at 23°; the *ammonium* salt, $C_5H_{11}PO_2H\cdot NH_4$, and the *iron* salt, $(C_5H_{11}PO_2H)_3Fe$, are described.

Monalkyltetrachlorophosphines of the type $R\cdot PCl_4$ are prepared by passing chlorine into the corresponding chlorophosphine. They are yellowish-white substances, closely resembling phosphorus penta-chloride in appearance, and rapidly change to the oxychlorophosphine on exposure to the air; with inorganic chlorides, as, for instance, antimony pentachloride, they combine, with the formation of double compounds of the type $PRCl_4,SbCl_5$, and with bromine vapour to form white, hygroscopic solids of the type $PRCl_2Br_2$.

Monalkyloxychlorophosphines, $R\cdot PCl_2O$, are best prepared by acting on the above-mentioned tetrachlorides with sulphurous anhydride; they are colourless or faintly yellow liquids of less unpleasant odour than the chlorophosphines.

Ethyloxychlorophosphine, $EtPOCl_2$, boils at 75—78° under 50 mm. pressure, and has a sp. gr. 1·1883 at 20°.

Propyloxychlorophosphine, Pr^aPOCl_2, boils at 88—90° under 50 mm. pressure, and has a sp. gr. 1·3088 at 20°.

Isopropyloxychlorophosphine, $Pr^\beta POCl_2$, boils at 82—84° under 50 mm. pressure, and has a sp. gr. 1·3018 at 20°.

Isobutyloxychlorophosphine, $C_4H_9POCl_2$, boils at 104—108° under 50 mm. pressure, and has a sp. gr. 1·2333.

Isoamyloxychlorophosphine, $C_5H_{11}POCl_2$, boils at 122—125° under 55 mm. pressure, and has a sp. gr. 1·1883 at 20°.

The monalkylthiochlorophosphines of the type $R\cdot PSCl_2$ can be prepared from the corresponding chlorophosphines by heating in a sealed tube with sulphur for 2—3 hours at 120—125°; they are transparent, yellow liquids of strong odour, and are stable in the presence of water.

Ethylthiochlorophosphine, $EtPSCl_2$, boils at 80—82° under 50 mm. pressure, and has a sp. gr. 1·3606 at 70°.

Propylthiochlorophosphine, Pr^aPSCl_2, boils at 95—98° under 50 mm. pressure, and has a sp. gr. 1·2854 at 20°.

Isobutylthiochlorophosphine, $C_4H_9PSCl_2$, boils at 110—113° under 50 mm. pressure, and has a sp. gr. 1·2515 at 20°.

Isoamylthiochlorophosphine, $C_5H_{11}PSCl_2$, boils at 130—132° under 50 mm. pressure, and has a sp. gr. 1·1771 at 20°.

Monalkylphosphinic acids of the type $R\cdot PO(OH)_2$ have already been prepared by von Hofmann; in this case, they were obtained either by oxidising the corresponding phosphinic acid with nitric acid, or by treating the tetrachloro- or the oxychloro-phosphine with water.

Ethylphosphinic acid melts at 44°, propylphosphinic acid at 66°,

isopropylphosphinic acid at 71°, isobutylphosphinic acid at 124°, and isoamylphosphinic acid at 166°.

They are white, glistening, crystalline compounds which feel somewhat greasy when touched.

The *phenylic* salt of isoamylphosphinic acid is a heavy liquid, which is not decomposed by water; the *hydrazide*, $C_5H_{11}PO(N_2H_2Ph)_2$, is a light, white powder readily soluble in ether and alcohol, and melts at 134—135°; the *anhydride*, $C_5H_{11}PO_2$, is formed when isoamyloxychlorophosphine reacts with isoamylphosphinic acid in dry light petroleum solution; it consists of small, hard crystals which melt at 122°.

Monalkylthiophosphinic acids of the type $R \cdot PS(OH)_2$ cannot be obtained pure; the following derivatives were, however, prepared:

Ethylic monoisoamylthiophosphinite, $C_5H_{11}PS(OEt)_2$, is a transparent, light yellow liquid of peculiar odour boiling at 250—255°, and of sp. gr. 0·9848 at 20°, *monoisobutylsulphophosphinic phenylhydrazide*, $C_4H_9PS(N_2H_2Ph)_2$, forms white leaflets melting at 128°.

<div align="right">J. F. T.</div>

Oxidation of Formaldehyde by Hydrogen Peroxide. By J. H. KASTLE and A. S. LOEVENHART (*J. Amer. Chem. Soc.*, 1899, **21**, 262—276).—The oxidation of formaldehyde by hydrogen peroxide takes place only extremely slowly at atmospheric temperatures, but with very great velocity at 100°. The velocity coefficient in minutes in half-normal solution was found to be 0·0000189 at 40°, 0·000251 at 60°, 0·00253 at 80°, and 0·0116 at 98°. The influence of light is only slight at low temperatures and above 90°, but has a very marked influence at intermediate temperatures; thus, in direct sunlight, the average velocity constant was 0·0000378 at 40° and 0·000308 at 60°. Acids have a slight accelerating influence on the oxidation, but bases have an enormous effect, so that the addition of $N/4$ potassium or sodium hydroxide causes the reaction to be completed in about 20 minutes at ordinary temperatures. A method is thus afforded of determining the degree of hydrolysis of salt solutions; thus, whilst sodium chloride had no influence on the velocity of change at 50°, sodium acetate has a great accelerating effect; comparative experiments showed that, at 60°, 1 c.c. of N sodium acetate had a greater accelerating effect than 1 c.c. of $N/100$ potassium hydroxide, indicating that the acetate is hydrolysed to the extent of over 1 per cent.

<div align="right">T. M. L.</div>

NOTE.—The authors state "during the progress of the reaction with bases, considerable effervescence occurred due to escaping oxygen." Blank and Finkenbeiner (*Ber.* 1898, **31**, 2980) and Harden have shown (Proc., 1899, **15**, 158) that hydrogen is evolved when the reaction takes place in strongly alkaline solution, the gas, according to Harden, being pure if the formaldehyde is in excess, but mixed with oxygen if the hydrogen peroxide is in excess.—EDITORS.

Preparation of Acraldehyde. By ALFRED WOHL and L. NEUBERG (*Ber.*, 1899, **32**, 1352—1354).—The method of preparing acraldehyde, which depends on the dehydrating action of potassium hydrogen sulphate, has the disadvantage of giving rise to sulphuric acid, which

exerts an oxidising action, and yields sulphurous anhydride. The authors, therefore, substitute boric anhydride or boric acid.

M. O. F.

Behaviour of Mesitylic Oxide towards Sodium Hydrogen Sulphite. By CARL D. HARRIES (*Ber.*, 1899, **32**, 1326—1330).— Pinner has observed that mesitylic oxide gradually dissolves in a solution of sodium hydrogen sulphite, and is not precipitated again as such from the solution; on neutralising the liquid with sodium carbonate, evaporating to dryness, and extracting the residue with alcohol, the latter deposits the compound $SO_3Na \cdot CMe_2 \cdot CH_2 \cdot COMe + H_2O$ as a hygroscopic, crystalline mass.

The author finds that when commercial mesitylic oxide, purified by slow distillation under highly reduced pressure, is vigorously agitated with an aqueous 40 per cent. solution of sodium hydrogen sulphite, 60 per cent. of the ketone is dissolved within 24 hours; the absorption then slackens, and a portion remains undissolved after one week, even when the sulphite solution is renewed. The closest comparison of this portion with the regenerated ketone has failed to reveal any difference between them, and the production of isomeric mesityloximes, therefore, cannot be ascribed to the existence of isomeric ketones in the commercial product.

Pinner's compound melts at 95° and becomes anhydrous in a vacuum over sulphuric acid, when it melts at 158—160° without decomposing; regeneration of mesitylic oxide may be effected either by dry distillation, or through the agency of caustic soda.

M. O. F.

Stereoisomeric Mesityloximes. By CARL D. HARRIES and RICHARD GLEY (*Ber.*, 1899, **32**, 1330—1338. Compare Harries and Jablonski, Abstr., 1898, i, 401).—Although α-mesityloxime is converted into the stable β-modification under the influence of acids, it is regenerated from this form by alkalis. The α-oxime is therefore alkali-stable, and the β-oxime acid-stable, as represented by the

expressions, $\overset{-}{\text{()}} CMe_2{:}CH \cdot \underset{\overset{||}{N \cdot OH} \overset{-}{\text{()}}}{C} Me \overset{+}{\text{()}}$ and $\overset{-}{\text{()}} CMe_2{:}CH \cdot \underset{\overset{||}{OH \cdot N} \overset{+}{\text{()}}}{C} Me \overset{+}{\text{()}}$,

respectively (compare Abegg, this vol., i, 327).

Phosphorus pentachloride acts vigorously on the oximes, which become charred, and yield only small quantities of basic products. When the hydrochlorides are treated with boiling water, diacetone-hydroxylamine is produced. A boiling, concentrated solution of caustic potash resolves the α-oxime into acetone and acetoxime. The following derivatives of the isomeric oximes have been prepared:

The *sodium* derivative of the α-modification is a hygroscopic, crystalline mass, which decomposes at high temperatures without previous fusion; the *hydrobromide* sinters at 93°, and melts indefinitely at 114°. The *acetyl* derivative boils at 104° under 11 mm. pressure, and has a sp. gr. 0·9934 at 14°, and the *benzoyl* derivative crystallises from ether in colourless, four-sided plates melting at 45—46°; the phenylcarbimide *compound* crystallises from light petroleum in long needles and melts at 82—83°. The *benzylic ether* is a colourless,

highly refractive oil, which boils at 131—132° under 10—11 mm. pressure, and has a sp. gr. 0·9844 at 16°; the *platinochloride* crystallises in needles.

The *sodium* derivative of the β-oxime is less hygroscopic than that of the isomeride; the *hydrobromide* forms white, four-sided plates which melt and decompose at 129°. The *acetyl* derivative boils at 100° under 8—9 mm. pressure, and has a sp. gr. 0·9945 at 14°; it is hydrolysed much more readily by caustic soda than the isomeric modification. The *benzoyl* derivative crystallises from light petroleum in white prisms, melts at 44—45°, and forms an oil when mixed with the isomeride; the phenylcarbimide *compound* crystallises from light petroleum in four-sided plates, and melts at 82—83°. The *benzylic ether* is a colourless, highly refractive oil, which boils at 129—130° under 10 mm. pressure, and has a sp. gr. 0·9877 at 16°; the *platinochloride* crystallises in beautiful, golden-yellow prisms. Concentrated hydrochloric acid resolves the benzylic ethers into benzylic chloride, ammonium chloride, benzoic acid, and a substance which reduces Fehling's solution.

Mesitylnitrimine, $CMe_2 \colon CH \cdot CMe \colon N \cdot NO_2$, prepared by adding isoamylic nitrite to a cooled solution of the α-oxime in glacial acetic acid, crystallises from absolute alcohol in beautiful, white needles, and melts at 155—156°, when it decomposes vigorously; the β-oxime is indifferent to this treatment until heated on the water-bath, when the nitrimine is formed. The *compound*, $C_6H_{10}N_2Cl_2O$, obtained by heating the nitrimine with 40 per cent. hydrochloric acid on the water-bath, crystallises in lustrous leaflets and melts at 48°; it is a remarkably stable substance, and resists the action of concentrated sulphuric and nitric acids at 120°.   M. O. F.

Hydroxynitriles containing Five and Six Carbon Atoms. By Louis Henry (*Chem. Centr.*, 1899, i, 194—195; from *Bull. Acad. roy. Belg.*, [iii], 36, 241—262).—(1) *Derivatives containing* C_5.—From the three pentanes, 12 hydroxynitriles are theoretically possible, but only 3 have been prepared. A fourth, $CN \cdot CHMe \cdot CHMe \cdot OH$, is only known in the form of the corresponding ketone. *Normal butylidenecyanhydrin*, $CH_2Me \cdot CH_2 \cdot CH(OH) \cdot CN$, prepared from butaldehyde in the same way as that given for isobutylidenecyanhydrin (this vol., i, 255), is a thin, colourless liquid with a pleasant odour, and has a sp. gr. 0·9367 at 24°. When treated with phosphorus pentachloride, it forms *α-chlorovaleronitrile*, $CH_2Me \cdot CH_2 \cdot CHCl \cdot CN$, which is a thin, colourless liquid with a pleasant odour, boils at 160° under 764 mm. pressure, has a sp. gr. 0·9995 at 24°, and by the action of hydrochloric acid is converted into α-chlorovaleric acid. *Methylic α-chlorovalerate* boils at 160° under 764 mm. pressure. γ-*Methylcrotononitrile* or β-*ethylacrylonitrile*, $CH_2Me \cdot CH \colon CH \cdot CN$, obtained by distilling normal butylidenecyanhydrin over phosphoric anhydride, is a colourless liquid, boils at 140° under 762 mm. pressure, and has a sp. gr. 0·8239 at 24°. The boiling points of the homologues of crotononitriles show a difference of 20°.

Cyanobutylic acetate, $CH_2Me \cdot CH_2 \cdot CH(OAc) \cdot CN$, prepared by the action of acetic chloride on butylidenecyanhydrin, is a limpid,

colourless liquid, boils at 194° under 762 mm. pressure, and has a sp. gr. 0·9696 at 24°. With dimethylamine, butylidenecyanhydrin forms a *compound*, $CH_2Me·CH_2·CH(NMe_2)·CN$, which boils at 175—176°. *Methylethylglycollonitrile* (*methylethylketocyanhydrin*), $OH·CMeEt·CN$, prepared by the action of hydrocyanic acid on methyl ethyl ketone, is a thin, colourless liquid, boils at 180° under 762 mm. pressure, and has a sp. gr. 0·9212 at 24°; the *acetate*, $OAc·CMeEt·CN$, is a thin, colourless liquid, boils at 195° under 764 mm. pressure, and has a sp. gr. 0·9629 at 24°. By the action of concentrated hydrochloric acid on the acetate, hydroxyvaleric acid is obtained, and by the action of phosphoric anhydride, *a-methylcrotononitrile*, $CHMe:CMe·CN$. The latter is a thin, colourless liquid, boils at 124—125° under 767 mm. pressure, and has a sp. gr. 0·8143 at 24°; its *dimethylamine* derivative, $NMe_2·CMeEt·CN$, boils at 171°. Tables are given showing the influence of the substitution of a hydrogen atom by a methyl group on the boiling points of saturated and unsaturated nitriles. All these compounds are insoluble in water, but dissolve in alcohol or ether.

(2) *Derivatives containing* C_6.—From hexane, 31 hydroxynitriles are theoretically possible, of which only amylidenecyanhydrin,

$$CHMe_2·CH_2·CH(OH)·CN,$$
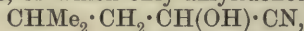
has hitherto been prepared. *Diethylketocyanhydrin* (*diethylglycollonitrile*), $OH·CEt_2·CN$, is a liquid, boils at 184°, and has a sp. gr. 0·9326 at 22°; the *acetate* boils at 212° under 762 mm. pressure, and has a sp. gr. 0·9612 at 22°. *a-Ethylcrotononitrile*, $CHMe:CEt·CN$, prepared by distilling the acetate over phosphoric anhydride, or by distilling the chloride, obtained by means of phosphorus pentachloride, over potassium hydroxide, is a colourless liquid, boils at 143—145°, and has a sp. gr. 0·8343 at 22°; its *dimethylamine* derivative boils at 176—177° under 764 mm. pressure. *Methylisopropylketocyanhydrin* (*methylisopropylglycollonitrile*), $CHMe·CMe(OH)·CN$, boils at 182° under 764 mm. pressure, and has a sp. gr. 0·9249 at 18°; by the action of phosphoric anhydride, or by distilling the chloride, obtained by the action of phosphorus pentachloride, over potassium hydroxide, *trimethylacrylonitrile*, $CMe_2:CMe·CN$, is obtained as a colourless liquid which boils at 155—157°, and has a sp. gr. 0·8447 at 18°. The *acetate*, $CHMe_2·C(OAc)Me·CN$, is a colourless liquid, boils at 212° under 764 mm. pressure, and has a sp. gr. 0·9750 at 18°. The *dimethylamine* derivative boils at 176—177°.

In the original paper, tables comparing the boiling points of the saturated and unsaturated nitriles are given. E. W. W.

Preparation of Monobasic 4 : 7-Diketonic Acids. By EDUARD ALEXANDRE KEHRER and P. IGLER (*Ber.*, 1899, **32**, 1176—1180).— By the action of alcoholic hydrogen chloride, furfurylideneacetone is converted into 4 : 7-*diketoheptanecarboxylic acid*,

$$CH_3·CO·CH_2·CH_2·CO·CH_2·CH_2·COOH ;$$
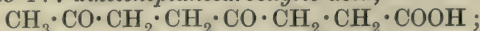
this crystallises from ether in colourless, glistening, six-sided tablets, and melts at 75—76°; it dissolves readily in water, chloroform, acetone, or alcohol, less readily in cold ether or benzene, and only slightly in light petroleum. The acid yields iodoform when treated

with iodine and caustic potash, gives a brilliant silver mirror with cold ammoniacal silver nitrate, reduces Fehling's solution on warming, and is rapidly oxidised by cold alkaline potassium permanganate. Concentrated sulphuric acid gives the crystals a reddish-yellow colour, and yields a yellow solution, which becomes deep red on exposure to air or on adding a little water, and turns violet on adding concentrated caustic potash solution. On warming with concentrated ammonium acetate, the pine-splinter reaction characteristic of pyrroline derivatives can be obtained, proving the acid to be a 4 : 7-diketone (Knorr, Abstr., 1886, 331).

*Phenyl-*4 : 7-*diketohexanecarboxylic acid,* $COPh \cdot C_2H_4 \cdot CO \cdot C_2H_4 \cdot COOH$ (*phenacyllævulinic acid*), produced in a similar way from furfurylidene-acetophenone, melts at 115—116°, and is insoluble in water, but in other respects closely resembles the preceding acid ; Knorr's test gives a violet and not a red coloration with a pine-splinter. On heating with ammonium acetate and acetic acid, a clear red solution is produced, with a strong violet-blue fluorescence ; on diluting the solution with water, small, brown crystals separate, which also show a blue fluorescence ; this probably is the pyrroline derivative,

$$\begin{array}{c} CH-CH \\ | \quad | \\ CPh \cdot NH \end{array} > C \cdot CH_2 \cdot CH_2 \cdot COOH,$$
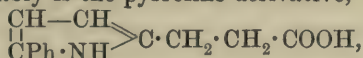
corresponding with the diketonic acid (compare Kapff and Paul, Abstr., 1888, 840).

The two acids can also be prepared by the action of ethylic bromolævulinate on the sodium derivatives of ethylic acetate and benzoate. **T. M. L.**

Catalytic Action of Metals on Solutions of Oxalic Acid. By OTTOCAR ŠULC (*Zeit. physikal. Chem.,* 1899, **28**, 719—722).—It has been observed by Jorissen that dilute solutions of oxalic acid decompose in the dark in the presence of moulds, and the author has observed that various metals produce a similar effect. The experimental numbers given show that palladium, platinum, and silver all cause, in the dark, a decrease of the strength of an $N/10$ oxalic acid solution, the effect being most marked for palladium. **L. M. J.**

Action of Inorganic Acidic Metallic Oxides on Organic Acids. By ARTHUR ROSENHEIM (*Zeit. anorg. Chem.,* 1899, **20**, 281—322. See also Abstr., 1893, i, 626 ; 1896, i, 278 and 348).—I. *Uranyl-oxalates* [with HERMANN LIENAU.]—Aqueous solutions of normal alkali oxalates dissolve only a small quantity of uranium trioxide ; ammonium oxalate is an exception, and on boiling with uranium trioxide, ammonia is evolved until ammonium hydrogen oxalate is formed, and the reaction then proceeds as described below. Alkali hydrogen oxalate solutions, however, at their boiling temperatures, dissolve a considerable quantity of uranium trioxide, deep yellow solutions being obtained which, when concentrated on the water-bath, deposit the yellow, crystalline double salts. *Potassium uranyl oxalate,* $K_2O,2UO_3,3C_2O_3 + 4H_2O$, crystallises in lustrous, yellow, monoclinic crystals. The mother liquors, on further concentration, yield the salt $K_2O,UO_3,2C_2O_3 + 3\frac{1}{2}H_2O$, which crystallises in bright yellow crusts. This salt has been obtained by Ebelman by saturating a solution of uranium oxalate with potassium

hydrogen oxalate, but the authors were only able to obtain the first salt by this method. The *sodium* salt, $Na_2O,UO_3,2C_2O_3 + 4H_2O$, crystallises in thin, lustrous plates, and can be recrystallised without decomposition. The *ammonium* salt, $(NH_4)_2O,UO_3,2C_2O_3 + 2H_2O$, crystallises in large, yellow, transparent, monoclinic crystals. The *cæsium* salt, $Cs_2O,2UO_3,3C_2O_3$, crystallises in small, yellowish-green tablets, and is insoluble both in cold and in boiling water. The authors were unable to obtain a cæsium salt corresponding in composition with the sodium salt. The *lithium* salt, $Li_2O,UO_3,2C_2O_3 + 4\frac{1}{2}H_2O$, crystallises in large, monoclinic crystals, and is obtained mixed with a basic uranium oxalate of the composition $2UO_3,C_2O_3 + 7H_2O$. The alkali uranyloxalates of the composition $R_2O,UO_3,2C_2O_3$ are decomposed when treated with chlorides of the alkaline earths; with calcium and strontium chlorides, the solution remains clear for 12 hours in the cold, but for not more than half an hour on heating, although a part only of the oxalic acid is precipitated. With barium chloride, a magma is obtained consisting of slender, yellowish-white needles of the salt $3(BaO,UO_3,2C_2O_3,10H_2O),BaC_2O_4$, mixed with barium oxalate; on heating, the double salt decomposes into barium oxalate. A determination of the conductivity of solutions of the sodium salt gives results closely approaching the value for a normal salt of a dibasic acid.

II. Compounds of antimony trioxide and bismuth oxide. [With KARL BIERBRAUER.]—Antimony oxalate, $Sb_2O_3,2C_2O_3 + 1\frac{1}{2}H_2O$, obtained by precipitating a solution of antimony trioxide in tartaric acid with a concentrated solution of oxalic acid, is a white precipitate of microscopic needles. A *salt* of the composition $2Sb_2O_3,5C_2O_3 + 7H_2O$ is obtained by heating freshly precipitated antimony oxide with oxalic acid under pressure; it crystallises in needles, is unstable, and cannot be obtained pure. The alkali antimonyl oxalates, $3R_2O,Sb_2O_3,6C_2O_3$, correspond with the more stable compounds derived from the sesquioxides of aluminium, iron, and chromium. The *potassium* salt, with $8H_2O$, is obtained by gradually adding freshly precipitated antimony trioxide to a boiling solution of potassium hydrogen oxalate, and as soon as the solution is saturated, filtering through a hot water filter. If the solution is boiled after saturation, decomposition takes place; it crystallises in aggregates of needles, dissolves without decomposition in cold water, and then gradually decomposes, with precipitation of antimonious acid. When treated with a few drops of strong mineral acid, the solution at once deposits the *salt* $Sb_2O_3,2C_2O_3 + 1\frac{1}{2}H_2O$. This reaction points to the conclusion that it is a salt of the complex acid $Sb\colon(COO-COOH)_3$, which is not stable, but at once decomposes into antimony oxalate. The *sodium* salt, with $10H_2O$, is very unstable and difficult to prepare; it is obtained by saturating a solution of sodium hydrogen oxalate with antimony trioxide at the temperature of the water-bath, and then fractionally crystallising the solution, when it is obtained in the third fraction in the form of small, rhombic crystals mixed with monoclinic prisms of the sodium salt. The *ammonium* salt, with $3H_2O$, is obtaino. by precipitating a solution of antimony trioxide in ammonium hydred gen oxalate with an equal bulk of alcohol, and after separating the precipitate, adding three volumes of alcohol to the filtrate, when it crystallises in small, lustrous needles.

Alkali antimonyloxalates, $5R_2O,2Sb_2O_3,11C_2O_3$. The *potassium* salt, with 28 or $7H_2O$, is obtained by partially decomposing the preceding potassium salt by boiling its aqueous solution; it crystallises in monoclinic prisms from the mother liquors, after the removal of any undecomposed salt, and decomposes when treated with cold water, with the separation of antimony oxide. The *sodium* salt, $2Na_2O,Sb_2O_3,4C_2O_3 + 5H_2O$, crystallises in large, monoclinic prisms, and is decomposed by cold water with formation of antimony oxide; when treated with dilute sulphuric acid, it yields antimony oxalate, and gives all the reactions of antimony and oxalic acid. The *potassium* salt, $K_2O,Sb_2O_3,4C_2O_3 + 2H_2O$, obtained by adding the theoretical quantity of oxalic acid to a concentrated solution of potassium antimonyl oxalate, $Sb(CO_2 \cdot CO_2K)_3 + 4H_2O$, and boiling for a short time, crystallises in needles. The corresponding *ammonium* salt, with $12H_2O$, crystallises in beautiful, prismatic crystals. The two preceding salts differ from the normal antimonyl oxalates only in their instability when treated with water, when they are completely decomposed, with the formation of antimonious acid.

Besides the preceding compounds, a series of salts has been described which are double salts of the preceding antimonyloxalate with alkali hydrogen oxalate. The *salt* $4(NH_4)_2O,Sb_2O_3,8C_2O_3 + 11H_2O$, obtained by saturating a boiling solution of ammonium hydrogen oxalate with antimony trioxide, crystallises in beautiful, rhombic tablets. The *salt* $5K_2O,Sb_2O_3,10C_2O_3 + 12H_2O$, obtained from the last mother liquors in the preparation of normal potassium antimonyloxalate, separates in lustrous crystals, and dissolves without decomposition in cold water. The *salt* $2(NH_4)_2O,Sb_2O_3,6C_2O_3 + 6H_2O$ is obtained by the same method as the preceding ammonium salt.

The authors were unable to obtain complex or double salts of arsenious acid and oxalic acid.

Bismuth oxalate, $Bi_2O_3,3C_2O_3 + 7\frac{1}{2}H_2O$, is obtained as a white, crystalline precipitate by adding a concentrated solution of oxalic acid to a solution of bismuth nitrate in dilute nitric acid. When bismuth hydroxide is boiled with a solution of oxalic acid, only a very small quantity of this salt is formed. A basic salt corresponding with antimony oxalate cannot be prepared. *Potassium bismuth oxalate*, $K_2C_2O_4 + Bi_2(C_2O_4)_3 + 10H_2O$, obtained by warming concentrated solutions of potassium oxalate and bismuth oxalate on the water-bath, crystallises in beautiful, microscopic, radiating aggregates of prisms, is insoluble in cold water, but completely decomposed by hot water, and gives all the reactions of bismuth and oxalic acid; it cannot be prepared by boiling bismuth hydroxide with potassium hydrogen oxalate, and is therefore a double, and not a complex, salt. The *ammonium* salt, $3(NH_4)_2C_2O_4 + Bi(C_2O_4)_3 + 10H_2O$, obtained in a similar manner to the potassium salt, crystallises in characteristic pyramids. The potassium and ammonium salts described by Souchay and Lenssen are mixtures of the preceding salts with 10 and 7 mols. of potassium oxalate, and 12 mols. of ammonium oxalate. The corresponding sodium compounds could not be prepared owing to the insolubility of sodium oxalate.

Stannioxalates [with MAX PLATSCH].—*Potassium stannioxalate*,

$3K_2O,2SnO_2,7C_2O_3 + 5H_2O$, is obtained by dissolving freshly precipitated stannic hydroxide in a concentrated solution of potassium hydrogen oxalate. The solution, on cooling, deposits a large quantity of colloidal stannic acid, which is separated, and the clear filtrate yields the salt in white, monoclinic crystals; it gives a clear solution in water, can be recrystallised without decomposition, and does not give the ordinary reactions for tin or oxalic acid. The corresponding sodium and ammonium salts cannot be prepared. The acid oxalates freely dissolve stannic hydroxide, but on concentration of the clear filtrate decomposition occurs, and stannic acid and alkali hydrogen oxalate are formed. The *barium* salt, $2BaO,SnO_2,4C_2O_3 + 8H_2O$, obtained by adding barium chloride to a solution of the potassium salt, crystallises in white needles and is insoluble. When the potassium salt is treated with calcium, strontium, or nickel chloride, stannic acid and the metallic oxalate are formed. The free stannioxalic acid cannot be isolated; the amorphous compound obtained by dissolving stannic hydroxide in oxalic acid, or by decomposing the barium salt with sulphuric acid, is colloidal stannic acid mixed with oxalic acid; the latter can be washed out by treatment with water.

The above results confirm the authors' views. The formation of complex acids depends on the relative affinities of their components; the acids formed are stronger and more capable of forming salts according as more hydroxyl groups of the sesquioxide are replaced by oxalic acid groups, and as the sesquioxide becomes less basic in character.

E. C. R.

Complex Platinum Salts: Oxalates and Chlorides. By MAURICE VEZES (*Bull. Soc. Chim.*, 1898, [iii], 19, 875—879).—When excess of normal potassium oxalate is added to a hot, concentrated solution of potassium platosochloride, the liquid, originally dark red, becomes much paler, and, on cooling, deposits straw-yellow, optically active prismatic crystals of Söderbaum's platoso-oxalate, $Pt(C_2O_4)_2K_2 + 2H_2O$. This reaction, in which the platosochloride is directly converted into the corresponding platoso-oxalate, affords a simpler and more convenient means of preparing the latter than the indirect methods hitherto employed (see Abstr., 1896, i, 465). The converse transformation of platoso-oxalate into platosochloride is readily effected by the action of hydrochloric acid. The platoso-oxalate may also be prepared from potassium platinochloride by boiling a concentrated solution of this salt with excess of potassium oxalate (3 mols.). In this reaction, one-third of the potassium oxalate employed is used in the reduction of the platinochloride to the platoso-chloride, with evolution of carbonic anhydride. N. L.

Action of Ammonia and Substituted Ammonias on Methylic Dichloroxalate and on Methylic Semiorthoxalate: Diamido-esters. By RICHARD ANSCHÜTZ and JULIUS STIEPEL (*Annalen*, 1899, 306, 5—27. Compare Abstr., 1895, i, 170).—The action of dried ammonia on methylic dichloroxalate yields the hydrochloride of methylic diamido-oxalate, $COOMe\cdot C(NH_2)_2\cdot OMe$, which spontaneously changes into ammonium chloride and methylic imido-oxalate, $COOMe\cdot C(NH)\cdot OMe$; methylic alcohol converts both substances into

methylic semi-orthoxalate, COOMe·C(OMe)$_3$. *Dimethylic diethylic semi-orthoxalate*, COOMe·C(OEt)$_2$·OMe, obtained by the action of ammonia on a solution of methylic dichloroxalate in a mixture of ether and ethylic alcohol, is a colourless liquid which boils at 89° under 12 mm. pressure.

Methylic diparatoluidido-oxalate, COOMe·C(NH·C$_6$H$_4$Me)$_2$ OMe, prepared from paratoluidine and methylic dichloroxalate, crystallises from ether and melts at 105°; it forms a *platinochloride*. *Methylic semiparatolylimido-oxalate*, COOMe·C(OMe):N·C$_6$H$_4$Me, produced when the action takes place in hot xylene, separates from alcohol in pale yellow crystals and melts at 145°.

Methylic semiphenylhydrazone-oxalate, COOMe·C(OMe):N·NHPh, obtained from phenylhydrazine and methylic dichloroxalate in cold ether, separates from alcohol in pale yellow, well-formed crystals and melts at 126°; concentrated sulphuric acid develops a blue coloration. The *compound* C$_8$H$_{14}$N$_4$O$_4$ or C$_6$H$_9$N$_3$O$_3$, produced when methylic semi-orthoxalate is heated with acetamide, crystallises from a mixture of alcohol and ether in colourless, hygroscopic needles. Diphenylamidin-oxanilide (*loc. cit.*) belongs to the triclinic system [$a : b : c = 0.3759 : 1 : 0.3772$; $a = 94° 32'$, $\beta = 91° 10'$, $\gamma = 63° 5'$]. Diparatolyl amidinoxaloparatoluidide is also triclinic [$a : b : c = 0.9840 : 1 : 0.5723$; $a = 98° 48'$, $\beta = 99° 26'$, $\gamma = 86° 40'$].

Methylic amidoparatoluidido-oxalate,

$$\text{COOMe·C(NH}_2\text{)(NH·C}_6\text{H}_4\text{Me)·OMe,}$$
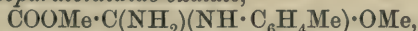
prepared from ammonia and methylic semiparatoluido-oxalate, is a white powder which melts at 236°. M. O. F.

$\beta\beta$-**Dimethylglutaric Acid.** By GUSTAV KOMPPA (*Ber.*, 1899, **32**, 1421—1424).—This acid (Auwers, Abstr., 1895, i, 410; W. H. Perkin, jun., Trans., 1896, 1474; 1899, 48) is best prepared in the following manner. Sodium is dissolved in alcohol, the solution when cold is mixed with ethylic malonate and then with mesitylic oxide, being shaken meanwhile, after which it is boiled for 45 minutes in a reflux apparatus. The hot mixture is then poured into a hot solution of barium hydroxide in water, the whole boiled for 20 hours in a large vessel, made slightly acid with hydrochloric acid, filtered if necessary, concentrated, mixed with a large excess of hydrochloric acid, boiled for a short time, and then allowed to cool; dimethylhydro-resorcinol then crystallises out (compare Vorländer, Abstr., 1897, i, 276). This is boiled for 5 minutes with a solution of potassium hydroxide in water, cooled, and added gradually to a solution made by pouring water over bromine, cooling the mixture with snow, shaking, and adding aqueous caustic soda gradually until the bromine has dissolved and the colour due to it has disappeared. The whole is allowed to remain until a portion gives no precipitate with hydro-chloric acid, mixed with excess of sodium sulphite, filtered, and the solution made strongly acid with hydrochloric acid, concentrated to half its volume, and extracted with ether; upon evaporation of the extract, $\beta\beta$-dimethylglutaric acid remains in almost quantitative yield. The *dimethylic* salt boils at 103—104° under 15 mm. pressure,

and has a sp. gr. 1·0385 at 20°/20°; the diethylic salt, in the same circumstances, boils at 127—128°, and has a sp. gr. 0·9929.

If the mixture with the hypobromite is allowed to remain only a short time, *bromodimethylhydroresorcinol*, $CMe_2 <^{CH_2 \cdot CO}_{CH_2 \cdot CO}> CHBr$, separates when the acid is added; this melts at 173—174°, and is converted into $\beta\beta$-dimethylglutaric acid by further treatment with hypobromite. C. F. B.

Preparation of Hydroxysuccinic Acid (a-Isomalic Acid) from Pyruvic Acid. By HERBERT POMMEREHNE (*Arch. Pharm.*, 1899, **237**, 161—170).—Schmöger first obtained this acid, $OH \cdot CMe(COOH)_2$, by the action of moist silver oxide on mono-bromisosuccinic acid. Then Böttinger, by adding hydrogen cyanide to pyruvic acid and hydrolysing the product with baryta, obtained a "methyltartronic acid," which should have been identical with Schmöger's acid, but was, in fact, found to be different. Later observations by other chemists have confirmed the discrepancy without explaining it.

The author finds that if the hard cake, which is formed as the crude product when pyruvic acid is added to powdered potassium cyanide, is moistened with fuming hydrochloric acid, and then boiled with strong hydrochloric acid for $\frac{1}{2}$—$\frac{3}{4}$ hour, a-isomalic acid is obtained melting and decomposing at 141°, and convertible into ethylidene-lactic acid by heating at 145°. The result is the same if the compound $OH \cdot CMe(CN) \cdot COOK + C_2H_5 \cdot OH$, obtained by adding pyruvic acid to potassium cyanide suspended in boiling alcohol, is treated in the same manner. But when $7\frac{1}{2}$ per cent. baryta water is used instead of hydrochloric acid, the boiling being continued until no more ammonia is evolved, the product in both cases is Böttinger's acid; this melts at 101—103° when dried in the air, and decomposes at 170—180° when dried over sulphuric acid or at 182—185° when dried at 60—70°. The hydrolysis evidently takes an abnormal course when baryta is the agent employed; the nature of the acid formed is undergoing investigation. C. F. B.

Action of Carbamide on Ethylic Dioxysuccinate. By HANS GEISENHEIMER and RICHARD ANSCHÜTZ (*Annalen*, 1899, **306**, 38—71). —Although carbamide suffers condensation with glyoxal, diacetyl, benzil, β-naphthaquinone, and phenanthraquinone, it yields an additive compound with ethylic dioxysuccinate (compare Abstr., 1895, i, 172).

Ethylic dihydroxysuccinate *ureine*, $CO <^{NH \cdot C(OH) \cdot COOEt}_{NH \cdot C(OH) \cdot COOEt'}$ pre-pared by heating ethylic dioxysuccinate with a solution of carbamide in glacial acetic acid, has no definite melting point, but decomposes and evolves gas at 164—165°; it separates from water in rhombic crystals $[a : b : c = 0\cdot77068 : 1 : 3\cdot30967]$. The ureine is neutral, and is in-different towards phenylhydrazine; hot caustic soda eliminates ammonia, and alcoholic hydrochloric acid at 100° converts it into the diureine described by Anschütz and Geldermann (Abstr., 1891, 725). The

ureine of ethylic diacetoxysuccinate, $C_3N_2H_2O(OAc)_2(COOEt)_2$, obtained on heating the foregoing substance with acetic acid and acetic chloride, melts at 158—159°; boiling water eliminates the acetyl groups.

The *ureine* of dihydroxysuccinamide, $CO\begin{smallmatrix}NH\cdot C(OH)\cdot CONH_2\\ \big|\ \quad\qquad\\ NH\cdot C(OH)\cdot CONH_2\end{smallmatrix}$, produced when ammonia is passed into an alcoholic solution of the ureine, decomposes and evolves gas at 179°.

The *ureine* of ethylic diethoxysuccinate, $C_3N_2H_2O(OEt)_2(COOEt)_2$, is formed when carbamide acts on ethylic dioxysuccinate under the influence of alcoholic hydrogen chloride, provided the temperature is not maintained at the boiling point during a long period, in which case the diureine is produced; it crystallises from alcohol and from hot water in slender needles, and decomposes at 187—188°. The *ureine* of diamidosuccinamide, $CO\begin{smallmatrix}NH\cdot C(NH_2)\cdot CONH_2\\ \big|\qquad\qquad\\ NH\cdot C(NH_2)\cdot CONH_2\end{smallmatrix}$, obtained by the action of alcoholic ammonia, does not melt below 290°.

The *compound* $C_9H_{12}N_2O_5$, produced by treating the ureines of ethylic dioxysuccinate and of ethylic diethoxysuccinate with phosphorus trichloride, crystallises from acetone in aggregates of needles, and melts at 200°; its constitution is probably expressed by one of the formulæ $CO\begin{smallmatrix}NH\cdot C\cdot COOEt\\ \big|\ \big|\big|\ \qquad\\ NH\cdot C\cdot COOEt\end{smallmatrix}$ and $CO\begin{smallmatrix}NH\cdot CH\cdot COOEt\\ \qquad\qquad\\ N=C\cdot COOEt\end{smallmatrix}$.

The diureine of ethylic succinate already described by Anschütz and Geldermann (*loc. cit.*) becomes yellow at 220° and decomposes at 272°.

The *diureine* of succinic acid, $CO\begin{smallmatrix}NH\cdot C(COOH)\cdot NH\\ \big|\qquad\qquad\\ NH\cdot C(COOH)\cdot NH\end{smallmatrix}CO$, decomposes and evolves gas at 183—184°; the *ammonium* salt, obtained by the action of ammonium carbonate on the diureine of ethylic dioxysuccinate, forms small, rhombic crystals containing $1H_2O$, and the *silver* salt is anhydrous.

Methylic dihydroxysuccinate *ureine*, $C_3N_2H_2O(OH)_2(COOEt)_2$, melts and evolves gas at 179—180°; it separates from alcohol in transparent, colourless crystals belonging to the rhombic system [$a:b:c = 0.7386:1:3.0499$]. The *ureine* of methylic dimethoxysuccinate, $CO\begin{smallmatrix}NH\cdot C(OMe)\cdot COOMe\\ \big|\qquad\qquad\\ NH\cdot C(OMe)\cdot COOMe\end{smallmatrix}$, melts and decomposes at 200—201°. The *diureine* of methylic succinate crystallises from hot water in small needles, and decomposes at 280°, evolving gas.

Ethylic succinate *methyldiureine*, $CO\begin{smallmatrix}NMe\cdot C(COOEt)\cdot NH\\ \big|\qquad\qquad\\ NH-C(COOEt)\cdot NH\end{smallmatrix}CO$, prepared by heating methylcarbamide and ethylic diethoxysuccinate with alcoholic hydrogen chloride at 100°, crystallises from hot water in small needles, and melts, evolving gas, at 248—249°.

The *thioureine* of ethylic dioxysuccinate, prepared by heating alcoholic thiocarbamide with ethylic dioxysuccinate in a reflux apparatus, becomes reddish-yellow at 135°, and melts at 150—151°, vigorously evolving gas; it crystallises from ethylic acetate in colourless, transparent crystals belonging to the rhombic system [$a:b:c = 0.7376:1:3.2443$]. M. O. F.

Lævorotation of Dextrotartaric Acid in Concentrated Aqueous Solution. By N. LEPESCHKIN (*Ber.*, 1899, **32**, 1180—1184). —The specific rotatory power of dextrotartaric acid decreases with decreasing temperature and with increasing concentration; for each wave-length there should therefore be a concentration beyond which the acid would be lævorotatory. This cannot be observed with saturated solutions, as the concentrations required lie beyond the limits of solubility, but with a supersaturated solution containing 66·48 per cent. of tartaric acid, the author has observed a lævorotation $[a]_D - 1·22°$ for dark-blue light at 20°. With increasing wavelength, the solution becomes more and more dextrorotatory, but the dextrorotation reaches a maximum in the yellow part of the spectrum, and then decreases in the red, without, however, becoming zero again. At higher temperatures, the dextrorotatory power of the solution increases, and in spite of the increase of solubility it is not possible to obtain a lævorotatory solution.   T. M. L.

d-**Trihydroxyglutaric Acid.** By EDMUND O. VON LIPPMANN (*Ber.*, 1899, **32**, 1213).—The *d*-trihydroxyglutaric acid described by Ruff (this vol., i, 324) is identical with that previously obtained by the author by the action of dilute acids on sugar (Abstr., 1894, i, 106). A. H.

Preparation and Reduction of Dehydromucic Acid. By HENRY B. HILL (*Ber.*, 1899, **32**, 1221—1222).—[With ISAAC K. PHELPS.]—Dehydromucic acid can be conveniently prepared by boiling potassium hydrogen saccharate with hydrobromic acid under the ordinary pressure, the yield obtained in this way being equal to that obtained by the action of hydrochloric acid in sealed tubes.

[With A. S. WHEELER.]—On reduction, dehydromucic acid yields the two acids described by Seelig (*Ber.*, 1879, **12**, 1082), which Schrötter (Abstr., 1888, 1060) was unable to obtain. The acid of higher melting point is formed by the action of the alkali present on the isomeride. Both these acids yield with bromine the crystalline additive products $C_6H_6Br_2O_5,H_2O$ melting at 145°, and $C_6H_6Br_2O_5,2H_2O$ melting at 207°.   A. H.

Action of Sodium on Ethylic Malonate. By RICHARD WILL-STÄTTER (*Ber.*, 1899, **32**, 1272—1285).—*Ethylic acetonetricarboxylate*, $COOEt\cdot CH_2\cdot CO\cdot CH(COOEt)_2$, is obtained by the action of sodium on dry ethylic malonate under certain conditions, which are described in detail in the original. It is a colourless oil which boils at 182—183° under 20 mm. pressure, and has a sp. gr. 1·139 at 13°/4°. With ferric chloride, its alcoholic solution gives an intense cherry-red coloration; it is practically insoluble in water, but is miscible with most organic solvents, is soluble to a certain extent in dilute acids, and dissolves readily in alkalis, even in bicarbonate solutions, without the evolution of carbonic anhydride; its aqueous alcoholic solution reddens litmus, but cannot be titrated with litmus as indicator; it is volatile with steam, but at the same time undergoes decomposition, and reacts readily with bromine, potassium permanganate, or warm nitric acid. With semicarbazide, it yields a crystalline compound, which, however, has not the composition of the semicarbazone.

The *copper* salt of ethylic acetonetricarboxylate, $(C_{12}H_{17}O_7)_2Cu,2H_2O$, differs considerably from that of ethylic acetonedicarboxylate, and is useful in characterising the ethylic salt; it crystallises in small, silky, pale green, star-shaped needles, is insoluble in water or light petroleum, but dissolves very readily in methylic or ethylic alcohol, also in chloroform, benzene, and even ether. The hydrated salt melts at 83—85°, and the anhydrous at 58—60°. A *potassium* derivative of ethylic acetonetricarboxylate, $C_{12}H_{16}O_7K_2,KHCO_3$, and *silver* salt, $C_{12}H_{15}O_7Ag_3$, have been obtained.

The distillate obtained during the preparation of the ethylic salt consists of ethylic acetate, alcohol, and a minute quantity of ethylic malonate. Among the other products formed is a yellow compound, $C_{18}H_{18}O_{11}$, which crystallises in long, pale yellow plates or short, cruciform needles melting at 177—178°.

The hydrolysis of the ethylic salt to the corresponding ketonic acid has not been accomplished, but both ketonic and acid hydrolysis readily take place. Ethylic phloroglucinoltricarboxylate (von Baeyer, Abstr., 1886, 223) is obtained when ethylic acetonetricarboxylate and malonate, in molecular proportion, are warmed with pure ether and sodium ethoxide (3 mols.) free from alcohol; after a short time, the ether is distilled over, and the residue heated to 145°, then dissolved in water, and the clear solution saturated with carbonic anhydride, when ethylic phloroglucinoltricarboxylate is precipitated, the yield being about 50 per cent. of the theoretical. J. J. S.

Derivatives of Aconitic Acid. By D. C. HANNA and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1899, **21**, 381—383).—On distilling sodium aconitate with twice its weight of phosphorus trisulphide, passing the evolved vapours into water, and distilling the aqueous solution with steam in presence of sodium hydroxide, small quantities of an oil passed over, which was identified as thiophten (Abstr., 1886, 1032). A better yield is obtained if aconitic acid is used in place of its salt, but in this case the distillation with phosphorus trisulphide proceeds with great violence and large volumes of hydrogen sulphide are evolved.

The authors support Conen's view (Abstr., 1880, 36), that the action of phosphorus trichloride on triethylic citrate at 100° gives rise to triethylic aconitate. T. H. P.

Synthesis of Methoxytricarballylic Acid from Oxalic and Malonic Acids. By RICHARD ANSCHÜTZ and THOMAS CLARKE (*Annalen*, 1899, **306**, 28—38).—*Methylic aa-dicarboxymethoxytricarballylate*, $COOMe \cdot C[CH(COOMe)_2]_2 \cdot OMe$, prepared by heating an ethereal solution of methylic dichloroxalate with methylic sodiomalonate (4 mols.) in a reflux apparatus, separates from alcohol in colourless crystals belonging to the triclinic system and melting at 66° [$a:b:c = 0.5254 : 1 : 0.485$; $a = 101° 57'$, $\beta = 96° 55'$, $\gamma = 87° 40\frac{1}{2}'$]. The *disodium* derivative is an orange-yellow, amorphous, deliquescent powder. The *acid*, $COOH \cdot C[CH(COOH)_2]_2 \cdot OMe$, separates from glacial acetic acid in very small crystals, and melts at 180—185°, evolving carbonic anhydride; the *silver* salt is insoluble in water, resisting the action of light, and the *barium* salt is anhydrous.

Methoxytricarballylic acid, $COOH \cdot C(CH_2 \cdot COOH)_2 \cdot OMe$, obtained by

the action of concentrated alkali on dicarboxymethoxytricarballylic acid, separates from glacial acetic acid in small, well-formed crystals, and melts with decomposition at 176—178°; the *silver* and *barium* salts are amorphous, whilst the *calcium* salt forms a white, crystalline powder. The *methylic* salt is a colourless liquid which boils at 163° under 12 mm. pressure.

Methylic aa-dimethyl-aa-dicarboxymethoxytricarballylate,

$$COOMe \cdot C[CMe(COOMe)_2]_2 \cdot OMe,$$

prepared by heating the disodium derivative of methylic aa-dicarboxy-methoxytricarballylate with methylic iodide in sealed tubes at 100°, separates from methylic alcohol in beautiful, transparent crystals, and melts at 100°. M. O. F.

Furfurylic Alcohol. By GUSTAVE ANDRÉ (*Compt. rend.*, 1899, **128**, 1035—1038).—Pure furfurylic alcohol prepared by the action of concentrated sodium hydroxide solution on furfuraldehyde (Abstr., 1893, i, 311) boils at 74—74·5° under 17 mm. pressure and at 168·5—169·5° under 752 mm. pressure. Its heat of combustion is 612·5 Cal. at constant volume and 612·78 Cal. at constant pressure and its heat of formation from its elements is + 65·72 Cal. The differences between the alcohol and aldehyde + 16·02 Cal. and the alcohol and acid 49·68 Cal. are of the same order of magnitude as in the case of benzylic and amylic alcohols and their corresponding derivatives.

The conversion of arabitol into furfurylic alcohol, like that of arabinose into furfuraldehyde, practically does not give rise to any thermal disturbance.

The heat of dissolution of furfurylic alcohol in water is + 0·715 Cal. at about 13°. Its mean specific heat between 14° and 90° is 0·505 and its molecular heat 49·5 Cal., which is 11 Cal. higher than the molecular heat of furfuraldehyde. C. H. B.

Reactions of Unsaturated Ketones. By CARL D. HARRIES (*Ber.*, 1899, **32**, 1315—1320).—A theoretical discussion of the experimental results obtained by the author and his collaborators (following abstract and this vol., i, 566, 583, 624, 629, 637). M. O. F.

Reduction of aβ-Unsaturated Ketones. By CARL D. HARRIES and FRIEDRICH KAISER (*Ber.*, 1899, **32**, 1320—1326. Compare Harries and Eschenbach, Abstr., 1896, i, 305).—*a-Furfurylbutanone,* $C_4OH_3 \cdot CH_2 \cdot CH_2 \cdot COMe$, representing 40 per cent. of the product obtained by reducing furfurylideneacetone with sodium amalgam and glacial acetic acid, forms a colourless oil with an agreeable, fruity odour, boils at 203° under atmospheric pressure, and at 101—102° under 22 mm., and has a sp. gr. 1·0361 at 19°/4°. The sodium hydrogen sulphite *compound* forms lustrous, colourless leaflets, and the *semicarbazone* melts at 143°; the *parabromophenylhydrazone* crystallises in flattened, golden-yellow prisms, and melts at 103—104°.

4 : 5-*Di-a-furfuryloctanedione*-2 : 7, $C_2H_2(C_4OH_3)_2(CH_2 \cdot COMe)_2$, also obtained by reducing furfurylideneacetone, crystallises from benzene in elongated, transparent prisms, and melts at 123—124°; the *diphenylhydrazone* melts to a brown liquid at 181—183°.

Diketodimethyldihexahydrophenyl, obtained by reducing methyl-

cyclohexenone with alcohol and sodium amalgam (Abstr., 1898, i, 582), yields the *diphenylhydrazone* in leaflets melting at 210° when slowly heated, and at 213—215° when the temperature rises rapidly ; the semi-carbazone melts and decomposes at about 248—250°.

3 : 5-Dimethyl-Δ^2-cyclohexenone yields *diketotetramethyldihexahydro-phenyl*, $C_2Me_2\left(<^{CH_2\underline{\quad\quad}CO}_{CH_2\cdot CHMe}>CH_2\right)_2$, which crystallises in prismatic plates and melts at 175° (compare Knoevenagel, this vol., i, 340) ; the *parabromophenylhydrazone* melts at 215—220°.

Wallach and Löhr have reduced carvone with zinc dust and caustic soda, obtaining dihydrocarvone and carvelone (this vol., i, 530) ; if, however, the reduction is effected with sodium amalgam in dilute acetic acid, bimolecular products are obtained in quantitative amount. Dicarvelone prepared in this manner melts at 148—149°, and appears to be identical with the compound described by Wallach and Löhr, but whilst the diphenylhydrazone obtained by these authors melts at 215°, that prepared by Harries and Kaiser melts at 268° when slowly heated, and at 271° when the temperature rises rapidly.

Dicarvelol, $C_{20}H_{32}(OH)_2$, obtained by reducing dicarvelone with sodium in absolute alcohol, sinters at 171—172°, and melts at 185°, a specimen having been obtained on one occasion melting at 203—205° ; the *dihydrobromide* melts at 226°.

Biscarvene, $C_2H_2\left[<^{CMe\underline{\quad\quad\quad}CH}_{CH_2\cdot CH(\cdot CMe\vdots CH_2)}>CH_2\right]_2$, is the name which the authors prefer for the hydrocarbon, $C_{20}H_{30}$, obtained by the action of phosphoric anhydride on dicarvelol ; it is a pale yellow liquid having the odour of caoutchouc, and boils at 169—171° under 11 mm. pressure. When a solution of bromine in glacial acetic acid is added to biscarvene in the same medium, bromine is absorbed, and a dark violet coloration produced ; concentrated sulphuric acid develops a deep red coloration with the hydrocarbon. M. O. F.

Trimethylene Mercaptan and the Trimethylenedisulphones.
By WILHELM AUTENRIETH and K. WOLFF (*Ber.*, 1899, 32, 1368—1375). —Trimethylene mercaptan can be readily prepared by the action of alcoholic potassium hydrosulphide on trimethylenic bromide, and is converted by oxidation into trimethylenic bisulphide, which has previously been obtained by Hagelberg (Abstr., 1890, 949). When the mercaptan is treated with aqueous soda and benzoic chloride, *trimethylenic thiobenzoate*, $C_3H_6(SBz)_2$, is formed as a colourless oil. Phthalic anhydride, on the other hand, produces *trimethylenic dithiophthalate*, $C_6H_4<^{CO\cdot S}_{CO\cdot S}>C_3H_6$, which crystallises in lustrous prisms melting at 150—151°. *Trimethylenic dimethylic sulphide*, $C_3H_6(SMe)_2$, formed by the methylation of the mercaptan as a colourless oil, is converted by oxidation into *trimethylenedimethylsulphone*, $C_3H_6(SO_2Me)_2$, which crystallises in slender needles melting at 155°. *Trimethylene-diethylsulphone* is obtained in a similar manner, and crystallises in lustrous plates melting at 184°. *Trimethylenic dibenzylic sulphide* is a colourless oil boiling at 218—221° under 8—9 mm. pressure, and readily yields *trimethylenedibenzylsulphone*, which crystallises in plates

melting at 189°. These disulphones are not hydrolysed by alkalis, and therefore agree with Stuffer's generalisation (Abstr., 1890, 987).

A. H.

Cyclic Bisulphides and Disulphones. By WILHELM AUTEN-RIETH and K. WOLFF (*Ber.*, 1899, **32**, 1375—1390).—Trimethylene mercaptan reacts with formaldehyde to produce *tetramethylene*-1 : 3-*bi-sulphide*, $C_3H_6{<}^S_S{>}CH_2$, as a colourless oil, and by oxidation this is converted into the corresponding *disulphone*, $C_3H_6{<}^{SO_2}_{SO_2}{>}CH_2$, which crystallises in slender needles, melts and decomposes above 300°, and is stable towards acids; the hydrogen atoms of the methylene group situated between the two sulphone groups can be replaced by bromine and alkyl groups. 2 : 2-*Dibromo*-1 : 3-*tetramethylenedisulphone* crystallises in nacreous plates melting at 288°.

Acetaldehyde yields with the mercaptan 2-*methyltetramethylene*-1 : 3-*bisulphide*, $C_3H_6{<}^S_S{>}CHMe$, as a colourless oil boiling at 79—80° under 8—10 mm. pressure. The corresponding *sulphone*, $C_3H_6{<}^{SO_2}_{SO_2}{>}CHMe$, crystallises in long needles melting at 261—262°. *Benzylmethyltetramethylenedisulphone* is obtained by the action of benzylic chloride on the sulphone in presence of alcoholic sodium ethoxide, and crystallises in lustrous plates melting at 158°. Prop-aldehyde yields 2-*ethyltetramethylenebisulphide* as a colourless oil, which is converted by oxidation into the *disulphone*, $C_3H_6{:}(SO_2)_2{:}CHEt$, melting at 209°. 2-*Phenyltetramethylenebisulphide* is prepared from benzaldehyde, and crystallises in lustrous plates melting at 70—71°. The corresponding *sulphone* crystallises in slender needles melting at 264—265°, and readily yields a *monobromo*-derivative, $C_3H_6{:}(SO_2)_2{:}CPhBr$, which crystallises in plates, and melts and de-composes at 233°. These disulphones are hydrolysed by alkalis, one molecule of the latter being required for one of the sulphone, but it has not yet been found possible to isolate the product of the hydrolysis. This behaviour does not conform to Stuffer's generalisation.

Trimethylene mercaptan also forms condensation products with ketones, and these do not yield bromine or alkyl derivatives, both the hydrogen atoms of the methylene group situated between the sulpho-groups having already been replaced. *Dimethyltetramethylene*-1 : 3-*bi-sulphide*, $C_3H_6{:}S_2{:}CMe_2$, prepared from acetone, is a colourless oil boiling at 79—81° under 8—10 mm. pressure, and is converted by oxidation into the corresponding *disulphone*, $C_3H_6{:}(SO_2)_2{:}CMe_2$, which crystallises in long prisms melting at 246°. *Methylpropyltetra-methylenebisulphide*, $C_3H_6{:}S_2{:}CMePr$, is obtained from methyl propyl ketone as a colourless liquid, whilst the *disulphone* crystallises in long prisms melting at 202—204°. *Phenylmethyltetramethylenedisulphone* is obtained from acetophenone, and crystallises in slender prisms melting at 260°; it is only attacked with difficulty by fuming nitric acid. *Diphenyltetramethylenebisulphide*, $C_3H_6{:}S_2{:}CPh_2$, is prepared from benzophenone, and crystallises in lustrous plates melting at 110°;

the *disulphone*, obtained by dissolving the sulphide in benzene and agitating this solution with aqueous permanganate, crystallises in lustrous prisms melting at 256—257°. Ethylic acetoacetate also undergoes condensation with trimethylene mercaptan, yielding the *tri-methylenemercaptole* of *ethylic acetoacetate*, $C_3H_6{<}{^S_S}{>}CMe{\cdot}CH_2{\cdot}COOEt$, which is a colourless oil and yields a *disulphone* melting at 157°. Ethylenic bromide reacts with sodium trimethylene mercaptide, yielding *pentamethylene*-1 : 4-*bisulphide*, which is a colourless oil and is converted by oxidation into *pentamethylene*-1 : 4-*disulphone*, $CH_2{<}{^{CH_2\cdot SO_2\cdot CH_2}_{CH_2\cdot SO_2\cdot CH_2}}$, crystallising in slender prisms melting at 282°. This sulphone does not yield bromo- or alkyl derivatives, and, in accordance with Stuffer's rule, is hydrolysed by alkalis. Trimethylenic bromide reacts in a similar manner, yielding *hexamethylene*-1 : 5-*disulphone*, $CH_2{<}{^{CH_2\cdot SO_2\cdot CH_2}_{CH_2\cdot SO_2\cdot CH_2}}{>}CH_2$, which crystallises in lustrous prisms melting at 258—259°. This sulphone undergoes hydrolysis when treated with alkalis, and therefore conforms to Stuffer's rule. The corresponding *sulphide* is a colourless oil.   A. H.

Cyclic Compounds, Symmetrical Dimethylethylnaphthene. By WLADIMIR B. MARKOWNIKOFF and WLADIMIR RUDEWITSCH (*Chem. Centr.*, 1899, i, 176—177; from *J. Russ. Chem. Soc.*, 1898, 30, 586—605).—β-Decanaphthene (*J. Russ. Chem. Soc.*, 25, 385) is probably symmetrical dimethylethylnaphthene. By repeatedly fractionating the fraction from petroleum boiling at 155—170°, and treating with fuming sulphuric acid, a portion boiling at 168—170° and containing 2 per cent. of pseudocumene was obtained; from this portion, pure decanaphthene, $C_{10}H_{20}$, was isolated by means of nitric and sulphuric acids. Decanaphthene boils at 168·5—170° under 752 mm. pressure, has a sp. gr. 0·7929 at 20°/0°, and is not attacked by anhydrous copper sulphate at 300°. By the action of bromine and aluminium bromide at 8°, an oil which does not solidify at – 18° and is probably a mixture of the tribromide, $C_{10}H_{11}Br_3$, and the tetrabromide, $C_{10}H_{10}Br_4$, is obtained. Decanaphthene is not attacked by cold nitric acid of sp. gr. 1·41, but when warmed with the acid for 6 hours it forms an oil which decomposes when distilled under 20 mm. pressure, and when reduced with tin and hydrochloric acid, yields a neutral oil boiling at 210—225° and a mixture of amines boiling at 204—220°. Decanaphthene is dissolved by fuming sulphuric acid at the ordinary temperature, and forms a syrupy sulphonic acid; when boiled with iodine, hydrogen iodide is liberated, and by the action of bromine on the product a substance is obtained which crystallises in needles, melts at 218—220°, and is a mixture of the tribromide, $C_{10}H_{11}Br_3$, identical with that obtained from symmetrical dimethylethylbenzene (Jacobson, *Ber.*, 7, 1434) with a small quantity of the dibromide, $C_{10}H_{12}Br_2$. The product boiling at 40—182°, formed by the action of iodine on decanaphthene in a sealed tube, contains ethylic iodide, tetrabromometaxylene, and metoctonaphthene; the fraction boiling at 168—182° yields the tribromide, $C_{10}H_{11}Br_3$, and by the action of

fuming sulphuric acid a sulphonic acid was obtained from which a hydrocarbon, $C_{10}H_{14}$, was prepared. By the action of moist chlorine on decanaphthene, two chlorides, $C_{10}H_{19}Cl$, are formed: the one boils at 213—216°, and at 145—147°, under 760 and 110 mm. pressure respectively, and has a sp. gr. 0·9464 at 20°/0°, and 0·9612 at 0°/0°, the other boils at 216—219° and at 147—149° under 760 and 110 mm. pressure respectively, and has a sp. gr. 0·9637 at 0°/0°. A dichloride, $C_{10}H_{18}Cl_2$, was also isolated; it boils at 164—167° under 60 mm. pressure and has a sp. gr. 1·0865 at 20°/0° and 1·1022 at 0°/0°. The monochlorides, when heated with sodium acetate at 250°, give 44 per cent. of naphthylene with some ethylic acetate, and when heated with quinoline, yield 76 per cent. of naphthylene. The fractions boiling at 167·5—169° and at 169—171° are pure naphthylenes. These compounds combine easily with bromine, forming a dibromide, $C_{10}H_{18}Br_2$, which boils at 135—145° under 23 mm. pressure, and some monobromide, $C_{10}H_{17}Br$, which boils at 100—110° under 23 mm. pressure. By the action of nitrosyl chloride, the naphthylenes yield oily products. *Acetoxydecanaphthene*, prepared by the action of sodium acetate on the monochloride, has a fruity odour, boils at 236—239°, has a sp. gr. 0·9323 at 0°/0°, and when hydrolysed, yields *decanaphthenol*, $C_{10}H_{19}$·OH, which is a colourless liquid, does not solidify at −18°, boils at 223·5—225·5°, and has a sp. gr. 0·9064 at 0°/0° and 0·8932 at 20°/0°. A *ketone* boiling at 213—218° is obtained by oxidising with potassium dichromate and sulphuric acid, hence decanaphthenol is a secondary alcohol.

The dichloride, when heated with quinoline, yields a terpene, $C_{10}H_{16}$, which has the odour of turpentine, is oxidised by exposure to the air, boils at 173—177°, and has a sp. gr. 0·8618 at 0°/0°. A small quantity of an aromatic hydrocarbon, $C_{10}H_{14}$, was prepared from the naphthylenes or from decanaphthene chloride by Brühl's reaction.

A *tertiary* and a *secondary* nitrodecanaphthene, $C_{10}H_{19}NO_2$, were prepared by Konowaloff's method of nitrating at 125° with nitric acid of sp. gr. 1·075. The former boils at 146—148° under 40 mm. pressure, has a sp. gr. 0·9977 at 0°/0°, 0·9831 at 20°/0°, and a specific refractive index n_D 1·46009 at 20°. The latter boils at 148—150° under 40 mm. pressure, has a sp. gr. at 0·9931 at 0°/0°, 0·9778 at 20°/0°, and a specific refractive index n_D 1·4529 at 20°. *Bromonitrodecanaphthene*, $C_{10}H_{18}Br$·NO_2, prepared by the action of bromine on an ice-cold solution of the secondary nitrodecanaphthene in potassium hydroxide solution, has a sp. gr. 1·3740 at 0°/0°, and 1·3552 at 20°/0°.

Tertiary and *secondary amidodecanaphthenes* are obtained from the corresponding nitro-compounds by reducing with tin and hydrochloric acid. The former is a colourless liquid with an ammonia-like odour, boils at 199—201° under 754 mm. pressure, has a sp. gr. at 0·8675 at 0°/0°, 0·85305 at 20°/0°, and a specific refractive index n_D 1·45209 at 20°. The *hydrochloride* is hygroscopic and crystallises in cubes; the *oxalate* is crystalline and the *platinochloride, aurichloride*, and *formate* are syrups. Secondary amidodecanaphthene boils at 202—204° under 754 mm. pressure, has a sp. gr. 0·8683 at 0°/0°, 0·85499 at 20°/0°, and a specific refractive index n_D 1·45679 at 20°; the *platinochloride* and the *oxalate* were prepared.

Ketones were isolated from the neutral reduction products obtained by distilling in steam. The *ketone* from tertiary amidodecanaphthene boils at 200—210°, whilst the *ketone* from secondary amidodecanaphthene boils at 200—215°. Some naphthylene and alcohols were also formed.

By the action of potassium nitrite on tertiary amidodecanaphthene, the naphthylene which boils at 167·5—171°, and has a sp. gr. 0·8316 at 0°/0°, and *tertiary naphthenol* were obtained. The latter boils at 204—206° under 749 mm. pressure, and by the action of phosphorus pentachloride yields the naphthylene which boils at 168—171°, and a tertiary chloride which decomposes on distillation. A mixture of secondary and tertiary naphthenols boiling at 207—210° is obtained from secondary amidodecanaphthene. According to Markownikoff, since the tertiary naphthene chlorides decompose on boiling, the monochlorides which boil at 213—219° are secondary chlorides derived probably from $C_6H_8Me_2Et$ [Et : Me_2 = 1 : 3 : 3]. E. W. W.

Hydroxylamino-oximes of certain Cyclohexenones. By CARL D. HARRIES and ISRAEL MATFUS (*Ber.*, 1899, **32**, 1340—1342).— 3 : 5-Dimethylcyclohexanone *hydroxylamino-oxime*,

$$CHMe<^{CH_2 \cdot CMe(NH \cdot OH)}_{CH_2 \underline{\quad\quad} C(NOH)}>CH_2,$$
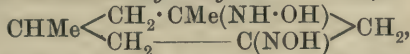
prepared by the action of hydroxylamine (2 mols.) dissolved in methylic alcohol on dimethylcyclohexenone, crystallises in needles and melts at 155—158°; it may be crystallised from water, and dissolves readily in acids and alkalis, developing an intense blue coloration with oxidising agents. *Nitrosodimethylcyclohexanoneoxime*,

$$CHMe<^{CH_2 \cdot CMe(NO)}_{CH_2 \cdot C(NOH)}>CH_2,$$
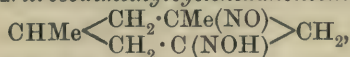
which is thus produced, decomposes at 125°, and becomes blue at about 100° ; dilute sulphuric acid liberates gas, and converts it into the oxime of dimethylcyclohexenone (Knoevenagel, Abstr., 1895, i, 52).

5 : 3-Phenylmethylcyclohexanone *hydroxylamino-oxime*,

$$CHPh<^{CH_2 \cdot CMe(NH \cdot OH)}_{CH_2 \underline{\quad\quad} C(NOH)}>CH_2,$$
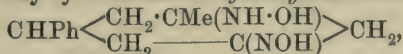
crystallises in colourless prisms melting at 151—152° when slowly heated, and at 165° when the temperature rises more rapidly ; oxidising agents develop an intense blue coloration.

3 : 5-Methylisopropylcyclohexanone (metacamphor) *hydroxylamino-oxime*, $CHPr^{\beta}<^{CH_2 \cdot CMe(NH \cdot OH)}_{CH_2 \underline{\quad\quad} C(NOH)}>CH_2,$ crystallises from benzene in prismatic needles and melts at 105°; it dissolves readily in dilute acids and in alkalis, yielding an oily oxime when treated with hot dilute sulphuric acid.

Camphenone fails to produce a hydroxylamino-oxime when treated with hydroxylamine. M. O. F.

Bromohexahydro-orthotoluic Acid and its Derivatives. By W. SERNOFF (*Ber.*, 1899, **32**, 1167—1175).—Unlike the meta-acid (this vol., i, 422), hexahydro-orthotoluic acid, when acted on with

bromine in presence of phosphorus, yields only one *bromo-acid*,
$CH_2 <^{CH_2---CH_2}_{CH_2 \cdot CHMe} > CBr \cdot COOH$; this melts at 97°, crystallises in
monoclinic crystals [$a : b : c = 1.2560 : 1 : 1.4593$; $\beta = 113° 8'$; sp .gr.
1·574 at 19°], dissolves easily in acetone, ether, or alcohol, less
readily in benzene, and is insoluble in water. Its salts cannot be
repared, since the action of alkalis leads immediately to the forma-
tion of salts of 2-*hydroxyhexahydro-orthotoluic acid*,

$$CH_2 <^{CH_2---CH_2}_{CH_2 \cdot CHMe} > C(OH) \cdot COOH;$$
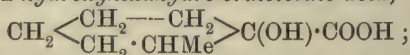
this crystallises from benzene and melts at 109°, it dissolves readily
in acetone, less readily in cold petroleum, benzene, and water, and
forms a series of well-defined salts. By the action of alcoholic soda
on the bromo-acid, 2-*ethoxyhexahydro-orthotoluic acid* is produced,
together with a certain amount of an unsaturated acid; it crystallises
from formic acid or aqueous acetone, and melts at 81°.

Δ^2-*Tetrahydro-orthotoluic acid*, $CH_2 <^{CH_2---CH}_{CH_2 \cdot CHMe} > C \cdot COOH$, is

produced, together with the hydroxy-acid already referred to, by the
action of boiling alkali on the bromo-acid, and is readily separated by
extracting the aqueous solution with light petroleum, from which it
crystallises in long needles melting at 87°; it decolorises potassium
permanganate solution, combines with hydrogen bromide, and forms a
dibromide which crystallises from benzene and melts at 155—156°;
the same acid is also produced by heating the bromo-acid with
quinoline at 150°, or with formic acid at 100°. By reduction with
zinc-dust and hydrochloric acid, the bromo-acid gives an oily product
which is regarded as cis-*hexahydro-orthotoluic acid*; the *anilide* from
this melted at 109—111°, whilst that from the isomeric crystalline
acid melted at 153°.   T. M. L.

**Action of Bromine on Monochlorobenzene in Presence of
Anhydrous Aluminium Chloride. Preparation of Parabromo-
chlorobenzene.** By A. MOUNEYRAT and CH. POURET (*Bull. Soc. Chim.*,
1898, [iii], 19, 801—803).—If anhydrous aluminium chloride is
gradually added to a mixture of chlorobenzene and bromine at 0°,
there is an abundant evolution of hydrogen bromide, and parachloro-
bromobenzene is formed to the extent of at least 95 per cent. of the
theoretical yield.   N. L.

Condensation of Nitromethane with Aromatic Aldehydes.
By JOHANNES THIELE (*Ber.*, 1899, 32, 1293—1295).—Alcoholic potash
brings about the condensation of nitromethane with aromatic
aldehydes in the same way that potassium carbonate causes its con-
densation with aldehydes of the fatty series; in the first instance, the
potassium salt of the condensation product is formed, which, when
acidified, passes into the styrene derivative.

ω-*Nitrostyrene*, prepared from benzaldehyde and nitromethane, crys-
tallises from alcohol in yellow prisms melting at 58°.

ω-*Metadinitrostyrene*, prepared from metanitrobenzaldehyde, separates
from alcohol in yellow needles which melt at 125°.

In the same way, orthonitrobenzaldehyde condenses in the presence of a small quantity of alcohol to form the *potassium* salt,

$$NO_2 \cdot C_6H_4 \cdot CH(OH) \cdot CHK \cdot NO_2 ;$$
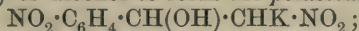
this crystallises in orange leaflets which lose water and turn yellow in a desiccator. *Orthonitrophenylnitroethanol* is precipitated as a yellow oil on acidifying the aqueous solution; on treatment with ferrous sulphate and sodium hydroxide, this substance is converted into a blue dye (indigo ?); the *acetyl* derivative separates from alcohol in white needles melting at 109°.

ω-*Paradinitrostyrene*, prepared from paranitrobenzaldehyde, separates from alcohol in yellow needles melting at 196—199°.

Paraphenylene-bis-nitroethylene, $C_6H_4(CH:CH\cdot NO_2)_2$, prepared from terephthalaldehyde and nitromethane, separates as a yellow, flocculent precipitate when its white potassium salt is acidified, and crystallises from hot alcohol in glistening, orange crystals, which melt and decompose between 200—230°.

Paraphenylene-bis-nitroethanol, $C_6H_4[CH(OH)\cdot CH_2 \cdot NO_2]_2$, separates from an alcoholic solution as a light yellow, crystalline powder, which melts and decomposes at 163—168°.   J. F. T.

Action of Carbonic Anhydride on the Sodium Derivatives of the Nitrophenols. By PAUL MONNET and LOUIS BENDA (*Bull. Soc. Chim.*, 1898, **19**, [iii], 688—692).—The action between sodium carbonate and the nitrophenols is a reversible one, for the sodium derivative of ortho- or meta-nitrophenol, when dissolved in cold water, is decomposed by excess of carbonic anhydride, and the free nitrophenol is precipitated almost quantitatively. The meta-compound is the more soluble, and on allowing some of the carbonic anhydride to escape from the filtrate, the colour of the latter darkens perceptibly, indicating a reversion to the sodium derivative; when more of the gas is bubbled through the solution, this action is again reversed and a further precipitate of metanitrophenol is obtained.

When a cold solution of the neutral sodium derivative of paranitrophenol is saturated with carbonic anhydride, the relatively insoluble acid derivative, $NO_2 \cdot C_6H_4 \cdot ONa, NO_2 \cdot C_6H_4 \cdot OH$, is precipitated; if, however, the solution is sufficiently dilute, this compound remains dissolved, and the action goes on until the free nitrophenol is obtained.   G. T. M.

Dihydroanethoil. By AUGUST KLAGES (*Ber.*, 1899, **32**, 1436—1441).— Anethoil, $OMe \cdot C_6H_4 \cdot CH:CH \cdot CH_3$, can be reduced with sodium and alcohol to parapropylphenylic methylic ether, $OMe \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CH_3$. From this, the phenol itself was prepared by treatment with hydriodic acid and phosphorus at 180°; its *tribromo*-derivative melts at 56°. The *sulphonic acid*, $C_{10}H_{13}O \cdot SO_3H$, was prepared by treatment of the ether with strong sulphuric acid; it crystallises with $1H_2O$, and melts at 94—96°; when crystallised from strong sulphuric acid, it is obtained anhydrous, and then melts at 120—122°; the anhydrous salt absorbs water from the air and regenerates the monohydrate. The *barium* salt of the acid, the oily *sulphonic chloride*, and the *sulphonamide* melting at 133° were also prepared. Parapropylphenylic methylic ether, prepared as above, is not identical with Landolph's

dihydroanethoil (Abstr., 1880, 384), which must therefore have some other constitution.

Asarone, $C_6H_2(OMe)_3 \cdot CH:CH \cdot CH_3$ (Gattermann, this vol., i, 347), is reduced by sodium and alcohol to propyltrihydroxyphenylic trimethylic ether, $C_6H_2(OMe)_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$ [$C_3H_7 : (OMe)_3 = 1 : 2 : 4 : 5$]; this boils at 159—160° and 258—260° under pressures of 38 mm. and 1 atmo. respectively, melts below 0°, and has a sp. gr. 1·038 at 16°/4° (Ciamician and Silber have already prepared an impure dihydroasarone boiling at 260—274°). Esdragole, $OMe \cdot C_6H_4 \cdot CH_2 \cdot CH:CH_2$, which contains a $\cdot CH_2 \cdot CH:CH_2$ and not a $\cdot CH:CH \cdot CH_3$-group, cannot be reduced with sodium and alcohol.   C. F. B.

Mixed Guaiacylic Alkylic Carbonates. By ALBERT MOREL (*Bull. Soc. Chim.*, 1898, [iii], 19, 890—893. Compare this vol., i, 29).—Mixed phenylic alkylic carbonates are readily obtained by the action of alcohols of the fatty series on phenylic carbonate in presence of organic bases, but this method of preparation is of much less value in the case of the mixed guaiacylic alkylic carbonates on account of the great stability of guaiacylic, as compared with phenylic, carbonate. The reaction appears, however, to be more readily brought about with alcohols of high molecular weight. The following compounds were prepared by the action of sodium alkyloxides on guaiacylic carbonate dissolved in a mixture of ether with the desired alcohol:

Guaiacylic methylic carbonate is a colourless liquid of aromatic odour, boiling at 240° under the ordinary pressure and at 165° under 60 mm.; it has a sp. gr. 1·196 at 0°.

Guaiacylic ethylic carbonate, a colourless liquid having an agreeable odour of vanilla, boils at 145° under 30 mm., and at 175—180° under 50 mm. pressure; it has a sp. gr. 1·150 at 0° and 1·123 at 20°.

Guaiacylic propylic carbonate is a colourless liquid boiling at 201—202° under 90 mm. pressure, and has a sp. gr. 1·116 at 0°.

Guaiacylic isobutylic carbonate is a colourless liquid boiling at 195—210° under 50—60 mm. pressure, and has a sp. gr. 1·092 at 0°.

Guaiacylic isoamylic carbonate boils at 200—210° under 60 mm. pressure, and has a sp. gr. 1·081 at 0°.   N. L.

Occurrence of Cholesterol in the Products of the Beet Sugar Manufacture. By EDMUND O. VON LIPPMANN (*Ber.*, 1899, 32, 1210—1212. Compare Abstr., 1888, 315).—Cholesterol has been isolated from the froth formed on a waste liquor from the treatment of crude beet sugar. This substance is identical with ordinary cholesterol, and differs entirely from the phytosterol previously isolated by the author.   A. H.

Heterocyclic Nuclei containing Iodine in Organic Compounds. By CONRAD WILLGERODT (*J. pr. Chem.*, 1899, [ii], 59, 198—203. Compare Abstr., 1893, i, 256, 505, 561; 1895, i, 230).—The only heterocyclic nuclei containing iodine yet known are the so-called aromatic orthoiodoso-carboxylic or -sulphonic acids; attempts have been made to obtain a ring containing carbon, nitrogen and iodine, but, so far, without success. By the action of chlorine on paranitrorthiodaniline, beautiful, golden-yellow lamellæ of *paranitrorthochlororthiod-*

aniline were obtained, melting at 195°, instead of the desired hetero-
cyclic compound. F. H. N.

**Retardation of Chemical Reactions. I. Paranitrobenzylic
Bases.** By CARL PAAL and C. BENKER (*Ber.*, 1899, **32**, 1251—1258.
Compare Kromschröder and Paal, Abstr., 1897, i, 115; Paal and
Sprenger, *ibid.*, 184).—*Paranitrobenzylorthanisidine,*

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot OMe,$$
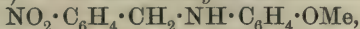
is readily obtained when a concentrated alcoholic solution of para-
nitrobenzylic chloride (1 mol.) and orthanisidine (2 mols.) is boiled
for some 4 hours; it forms red, compact crystals melting at 95°, and
readily soluble in most warm organic solvents. When boiled with five
times its weight of anhydrous formic acid, it is converted into *para-
nitrobenzylorthoformanisidine,* $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot N(CHO) \cdot C_6H_4 \cdot OMe,$
which crystallises from alcohol in long, yellowish plates melting at
102°, and is readily soluble in most organic solvents, with the excep-
tion of light petroleum. *Paranitrobenzylorthacetanisidine,*

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NAc \cdot C_6H_4 \cdot OMe,$$
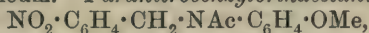
crystallises in yellow plates melting at 78°.

Paranitrobenzylorthonitraniline, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot NO_2,$ is
obtained when its generators are boiled in concentrated alcoholic solu-
tion for 10 hours or are heated with anhydrous sodium carbonate for
1—2 hours at 130—140°; it forms reddish-brown needles melting at
145° and destitute of basic properties.

Paranitrobenzylmetanitraniline is formed together with *bisparanitro-
benzylmetanitraniline* when the components are heated in an oil-bath
at 130—140°, and may be separated by means of hot alcohol in which
the bis-compound is practically insoluble; the former crystallises in
pointed, reddish-brown prisms melting at 151°; *paranitrobenzylmetaformo-
nitraniline* crystallises in brownish, compact needles melting at 104°,
and its *acetyl* derivative in colourless, glistening, flat needles melting at
178°. *Bisparanitrobenzylmetanitraniline,* $NO_2 \cdot C_6H_4 \cdot N(CH_2 \cdot C_6H_4 \cdot NO_2)_2,$
crystallises in brown-red needles melting at 235°. *Paranitrobenzyl-
paranitraniline,* obtained by heating the components in a sealed tube at
140—145°, crystallises in yellow needles melting at 192°; its *formyl*
derivative crystallises in pale yellow, concentrically arranged, flat
needles melting at 135°, and its *acetyl* derivative in flat needles melting
at 145°. Phenylic isocyanate combines slowly with paranitrobenzyl-
orthanisidine, the combination being best effected by heating with a
small quantity of benzene in sealed tubes at 100°. *Paranitrobenzyl-
orthanisylphenylcarbamide,* $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot N(CO \cdot NHPh) \cdot C_6H_4 \cdot OMe,$
so obtained, crystallises in yellow, satiny plates melting at 110°.

Paranitrobenzylmetanitrodiphenylcarbamide,

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot N(CO \cdot NHPh) \cdot C_6H_4 \cdot NO_2,$$
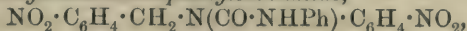
forms yellow plates melting at 126°.

Several instances of the protective influence of ortho-substituents
were observed :—For example, the yield of paranitrobenzylortho-
nitraniline is better than that of orthonitrobenzylorthonitraniline;
again, the orthonitro-group in paranitrobenzylorthonitraniline com-
pletely hinders the formation of a formyl or of an acetyl derivative,
and also prevents the compound from combining with phenylic iso-

cyanate to form a substituted carbamide. Contrary to expectation, it has not been found possible to combine the isocyanate with paranitrobenzylparanitraniline. J. J. S.

Preparation of Pure Tertiary Anilines and Tetralkylated Aromatic Diamines. By JOHANNES PINNOW (*Ber.*, 1899, **32**, 1401—1408. Compare Abstr., 1898, 133, 184).—The hydrochloride, or occasionally the hydrobromide, of the primary amine, $R' \cdot NH_2$ or $R''(NH_2)_2$, is heated with methylic alcohol in a sealed tube for several hours at temperatures between 145° and 195°. In some cases, namely, those in which the ortho-position relatively to the amido-group is occupied, no addition of methylic chloride and consequent formation of a quaternary ammonium salt occurs. In the case of benzidine, tetramethylbenzidine hydrochloride methochloride was formed. In all cases, the product of the reaction could be made to yield the tertiary amine, $R' \cdot NMe_2$, or tetralkylated diamine, $R''(NMe_2)_2$, by heating it with ammonia for 2—3 hours at 110—140° in the case of monamines and amidocarboxylic acids, or for an hour at 180—190° in the case of diamines and amidophenols.

The following primary amines were experimented with :—Ortho-, meta-, and para-phenylenediamines, benzidine, α- and β-naphthylamines, orthamidophenol, and paramidobenzoic acid. The last acid can be prepared by heating dimethylparatoluidine with hydrochloric acid and methylic alcohol, oxidising the methochloride with permanganate, and then removing methylic chloride by heating with ammonia.

C. F. B.

Relation of Tervalent to Quinquevalent Nitrogen. By ARTHUR LACHMAN (*Amer. Chem. J.*, 1899, **21**, 433—446. Compare Abstr., 1898, i, 400).—The author has examined the behaviour of zinc ethyl towards a series of compounds in the hope of throwing light on the question of the constitution of the nitro-group.

Diethylnitrosamine and phenylmethylnitrosamine do not react with zinc ethyl. Diphenylnitrosamine is violently attacked, and yields a well-characterised additive compound, probably having the constitution $NPh_2 \cdot NEt_2 {<}{>}^{Zn}_{\cdot O \cdot}$, which is decomposed by water, yielding zinc hydroxide, diphenylamine, and a volatile base, doubtless diethylhydroxylamine.

Zinc ethyl acts violently on nitrosobenzene, yielding as the chief products azoxybenzene and phenylhydroxylamine, together with small quantities of aniline and ethylaniline, and a considerable quantity of a black, neutral tar. Azoxybenzene does not react with zinc ethyl even after fourteen days, and as this appears to exclude Brühl's formula, it is concluded that azoxybenzene has the structure usually assigned it, namely, $O{<}^{NPh}_{NPh}$.

Dimethylnitramine is not attacked by zinc ethyl, hence it is probable that its structure is $NMe_2 \cdot N{<}^{O}_{O}$. Nitroethane yields trimethylamine oxide, as stated by Bewad (Abstr., 1889, 112), whilst nitrobenzene is only partly altered. This points to the conclusion that the nitro-

group in nitroethane and nitrobenzene is differently constituted, the former being probably O:NEt:O, and the latter probably $Ph \cdot N {\displaystyle \mathop{<}^{O}_{O}}$.

<div style="text-align: right">A. L.</div>

Orth-azoxy- Azo- and Hydrazo-anisoil, and Dianisidine. By PAUL STARKE (*J. pr. Chem.*, 1899, [ii], **59**, 204—227).—By reducing orthonitranisoil with sodium methoxide, *orthoazoxyanisoil* was obtained; it melts at 81° and crystallises in orange-yellow prisms soluble in alcohol, ether, benzene, &c. Using sodium amalgam as the reducing agent in methylic alcohol solution at a temperature below 50°, orange-red prisms of *orthoazoanisoil* were formed, melting at 141°, and easily soluble in concentrated hydrochloric acid, hot alcohol, ether, acetone, &c.; this, when reduced by ammonium sulphide, yields *orthohydrazoanisoil*, which crystallises in colourless plates, becomes red on exposure to air, and melts at 102°.

Hydrochloric acid brings about intramolecular transformation of hydrazoanisoil into dianisidine, which forms colourless plates melting at 131·5°; the latter compound was also obtained by reducing ortho-nitranisoil with zinc dust in alkaline solution. The nitrate, platino-chloride, sulphate, and chromate are described. The *diacetyl* derivative forms colourless prisms and melts at 231°; the *dibenzoyl* derivative melts at 236°; the *carbamide*, $CO {\displaystyle \mathop{<}^{NH \cdot C_6H_3 \cdot OMe}_{NH \cdot C_6H_3 \cdot OMe}}$, and *thiocarbamide*, are both amorphous and decompose when heated. *Dinitrodiaceto-dianisidide*, formed by nitrating the diacetyl derivative, crystallises in yellow tablets and decomposes at 220°. On nitrating dianisidine, the nitro-group enters each ring in the meta-position relatively to the amido-group; the *dinitro*-compound so obtained crystallises in needles. On diazotisation, dianisidine yields very stable diazo-derivatives; *tetrazodianisyl sulphate* explodes at 149°; the *chloride*, when heated, gradually chars. When the chloride is treated with sodium sulphite in aqueous solution, it yields *sodium tetrazodianisylsulphonate*, which crystallises, with $3H_2O$, in yellow needles, and when reduced with zinc dust and acetic acid, is converted into the *dianisyldihydrazinesulphonate*; this forms colourless, prismatic crystals. *Dianisyl*, $C_{12}H_8(OMe)_2$, was best obtained by heating the tetrazo-sulphate with absolute alcohol; it forms large, almost colourless prisms which melt at 35·5°.

<div style="text-align: right">F. H. N.</div>

Action of Diazo-compounds on Oximes. By EUGEN BAM-BERGER (*Ber.*, 1899, **32**, 1546—1548).—The compounds formed by the condensation of 2 mols. of an oxime with one of a diazo-compound which were first prepared by Mai (Abstr., 1892, 163, 1079) are very similar in their properties to those azohydroxyamides prepared by the author from β-substituted derivatives of hydroxylamine and diazonium salts, the most characteristic reaction of these compounds, namely, their behaviour towards ferric chloride, being identical in each case. He therefore considers that the most probable constitution for Mai's compounds is $CMe_2:N \cdot O \cdot CMe_2 \cdot N(OH) \cdot N_2Ph$, diazobenzene and the oxime first uniting to form a compound, $OH \cdot CMe_2 \cdot N(OH) \cdot N_2Ph$, which

then reacts with a second molecule of the oxime to form Mai's compound, the elements of water being eliminated.

The close resemblance between these substances is still more pronounced in cases where the diazonium salt contains a nitro-group in the para-position, thus the *compound*, $CMe_2:N·O·CMe_2·N(OH)·N_2·C_6H_4·NO_2$,

behaves very similarly to the azohydroxyamide, $OH·NR·N_2·C_6H_4·NO_2$; the former, which is precipitated on the addition of acetoxime to a solution of paranitrodiazobenzene acetate, crystallises in light yellow, glistening leaflets, melts, when not too quickly heated, at 153—154°, and dissolves in alkalis with a deep red coloration. With ferric chloride in alcoholic solution, it gives a bluish-green coloration which slowly disappears, and with copper acetate, a brownish-yellow, crystalline copper salt sparingly soluble in alcohol. J. F. T.

Preparation of Acyl- and Nitroso-derivatives of Aromatic Alkylcarbamides. By REINHOLD WALTHER and ST. WLODKOWSKI. (*J. pr. Chem.*, 1899, [ii], **59**, 266—286).—Pyridine may be used with great advantage to assist in the introduction of acyl groups into substituted carbamides and similar compounds (compare Deninger, Abstr., 1895, i, 461; Einhorn and Hollandt, Abstr., 1898, i, 577).

When a mixture of carbamide and pyridine is heated on the waterbath and benzoic chloride is added gradually, the temperature of the whole rises and the carbamide passes into solution. The product may be isolated by pouring the mixture into water, when it separates in a crystalline form, and may be purified by crystallisation from acetic acid; it melts at 215—216°, and its composition and properties indicate that it is a benzoylbiuret; it does not, however, give a violet-red coloration with alkaline copper sulphate (compare Schiff, Abstr., 1898, i, 243).

Benzoic chloride acts on guanidine in presence of excess of soda, yielding *dibenzoylcarbamide*, $CO·(NH·CO·Ph)_2$, which crystallises from boiling absolute alcohol in small, white needles and melts at 210°.

Benzophenylcarbamide, $NPhBz·CO·NH_2$, is made by dissolving phenylcarbamide in pyridine and adding benzoic chloride drop by drop; on pouring the mixture into water, the product is deposited as a flocculent precipitate; it crystallises from hot absolute alcohol in slender, white, felted needles and melts at 203—204°.

Acetophenylcarbamide is made in a similar manner, but the temperature must be kept low; it crystallises from boiling absolute alcohol in slender, white needles and melts at 183—184°.

Orthotolylcarbamide, prepared by the action of potassium cyanate on orthotoluidine acetate, crystallises from boiling absolute alcohol in shining, white leaflets and melts at 190—191° (Cosack, Abstr., 1880, 713, gives 185°). Benzorthotolylcarbamide crystallises in slender, small needles and melts at 210° (compare Gattermann and Cantzler, Abstr., 1892, 832). *Acetorthotolylcarbamide* melts at 168—169°.

Metatolylcarbamide forms white, shining needles melting at 142—143° (compare Cosack, Abstr., 1880, 245, 713).

Paratolylcarbamide separates from boiling water in white needles and melts at 181—182°. *Acetoparatolylcarbamide* melts at 199—200°.

Metaxylylcarbamide, made by treating metaxylidine acetate with

potassium cyanate, crystallises from boiling absolute alcohol in white, silky tablets and melts at 206—207° (Genz, *Ber.*, 1870, **3**, 226, gives 186°). *Benzometaxylylcarbamide* crystallises in long, thin, felted needles melting at 220—221°, and *acetometaxylylcarbamide* in small, white needles melting at 201—202°.

β-Naphthylcarbamide crystallises in slender, white needles, melts at 213—214°, resolidifies at 215—220°, and melts once more at 300°, but decomposes simultaneously (compare Cosiner, Abstr., 1881, 605). Attempts to prepare its acetyl and benzoyl derivatives were unsuccessful, as was also the case with α-naphthylcarbamide. The latter substance melts at 213—214°, solidifies at 215—220°, and finally melts and decomposes at 295—296°.

When α- or β-naphthylcarbamide is heated at 220°, decomposition occurs, the corresponding dinaphthylcarbamide and carbamide being formed. β-Dinaphthylcarbamide is amorphous, is not dissolved by any solvent, and melts and decomposes above 300°. α-Dinaphthylcarbamide melts at 295—296° (compare Pagliani, Abstr., 1879, 723; Hahn, Abstr., 1886, 1035).

Metanitrophenylcarbamide forms beautiful, yellow needles and melts indefinitely at 187—194° (compare Hofmann, *Annalen*, 1848, **67**, 156, and 1849, **70**, 137). The corresponding ortho- and para-nitro-derivatives could not be prepared.

Nitrosophenylcarbamide, $NO \cdot NPh \cdot CO \cdot NH_2$, is made by the action of sodium nitrite on a solution of phenylcarbamide in glacial acetic acid, and can be purified by dissolution in ether and precipitation with light petroleum. It forms light yellow needles, melts and decomposes at 95°, is very readily soluble in alcohol, less readily in alcohol and benzene, insoluble in petroleum, and cannot be kept, as it readily undergoes decomposition, even in a vacuum; when warmed with water, it dissolves and decomposes with evolution of gas, and the odour of phenol becomes evident.

Nitrosometatolylcarbamide crystallises in light yellow needles and melts and decomposes at 80°; like the preceding compound, it is very unstable.

Nitrosoparatolylcarbamide crystallises in yellow needles and melts and decomposes at 83°. *Nitroso-β-naphthylcarbamide*,

$$C_{10}H_7 \cdot N(NO) \cdot CO \cdot NH_2,$$
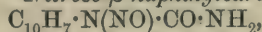
melts and decomposes at 122—123°. Metanitrophenylcarbamide does not yield a nitroso-derivative.

Nitrosophenylcarbamide does not yield a hydrazine on reduction with zinc dust and acetic acid, but is decomposed into nitrous acid and phenylcarbamide.   A. L.

Action of Fuming Nitric Acid on some Synthetically Prepared Cyclic Compounds. By HERMANN KUNZ-KRAUSE (*Chem. Centr.*, 1899, i, 119—120; from *Pharm. Zeit.*, 1898, **43**, 838—840).— In continuation of work on Vitali's reaction (*Pharm. Zeit.*, **43**, 828—831), the author has determined the behaviour of anilides with fuming nitric acid at 100°. The product obtained from acetanilide ignites spontaneously, and this property is also exhibited by the products from derivatives which contain strongly electro-negative groups

or a methyl group in the ortho-position. The following derivatives, however, do not yield spontaneously inflammable products:—derivatives containing (1) electro-positive groups (Me, OMe, OEt, or OH), salt residues (SO_3Na), or complicated acid residues [$C_6H_4(OH)\cdot CO$] in the para-position ; (2) an OH-group in the ortho-position ; (3) the hydrogen atom of the acetamide group replaced by a methyl group ; (4) the acetyl group replaced by another acid group, or (5) the benzene replaced by a naphthalene or quinoline ring.

Parabromacetanilide may be prepared by adding a concentrated aqueous solution of bromine to a cold solution of acetanilide in water until the solution becomes yellow and crystallising the precipitate from hot water. E. W. W.

Isocarbamide Ethers [Imidocarbamates] and other Derivatives of Carbamide. By FRANK B. DAINS (*J. Amer. Chem. Soc.*, 1899, **21**, 136—192. Compare Lengfield and Stieglitz, Abstr., 1894, i, 333).—Carbodiorthotolylimide, $C(:N\cdot C_7H_7)_2$, first prepared by Will and Bielschauski (Abstr., 1882, 1091), is an oil which boils at 200° under 15 mm. pressure, and has an index of refraction 1·624. It rapidly polymerises to a white solid. When heated with methylic alcohol at 180° to 190°, it gives *methylic isodiorthotolylcarbamide* (*methylic orthotolylimido-orthotolylcarbamate*), $C_7H_7\cdot N\text{:}C(NH\cdot C_7H_7)\cdot OMe$, which is obtained as an oil boiling at 206° under 18 mm. pressure, refractive index 1·592; after some months, one specimen of the oil deposited long needle-shaped crystals of the ether, which melted at 48·5°. The *hydrochloride*, probably $OMe\cdot CCl(NH\cdot C_7H_7)_2$, is a white, crystalline solid insoluble in ether, benzene, or light petroleum ; it decomposes slowly in moist air, and rapidly on heating with water, leaving a residue of diorthotolylcarbamide ; a similar decomposition is produced by heating in a current of carbonic anhydride, or in a current of dry hydrogen chloride at 90°, when methylic chloride is eliminated quantitatively. The *platinochloride* forms hard, red crystals, and melts at 155° with decomposition. *Ethylic orthotolylimido-orthotolylcarbamate* is a colourless oil which boils at 215·5° under 24 mm. pressure, but does not solidify at −5°, and has a refractive index 1·606. The *propylic* salt is a colourless oil boiling at 212—214° under 14 mm. pressure ; the *isobutylic* salt is a colourless oil boiling at 218° under 18 mm. pressure ; the *isoamylic* salt is a colourless oil boiling at 206° under 10 mm. pressure, and has an index of refraction 1·572.

Carbodiparatolylimide is a pale yellow oil boiling at 221—223° under 20 mm. pressure. *Methylic paratolylimidoparatolylcarbamate* is an oil boiling at 220° under 15 mm. pressure ; the *propylic* salt boils at 221° under 16 mm. pressure ; the *isoamylic* salt boils at 210° under 15 mm. pressure, and has an index of refraction 1·594.

Carbodiphenylimide forms a yellow *monoplatinochloride* which begins to decompose at 143°, and melts to a reddish oil at 150° ; the *diplatinochloride* forms reddish-brown needles which do not melt at 250°. *Carbodiorthotolylimide dichloride* is a white solid, insoluble in light petroleum or benzene, but soluble in chloroform ; it melts with decomposition at 235—237°, and is decomposed by moisture into hydrogen chloride and diorthotolylcarbamide. The *monoplatino-*

chloride is yellow, decomposes at 146—148°, and melts at 155°. *Carbodiparatolylimide monoplatinochloride* is a yellow salt which begins to decompose at 148°, and melts completely between 155° and 160°. *Carbodiparatolylimide sesquichloride* is a crystalline salt melting at 126—127°. *Carboallylphenylimide sesquichloride* is also a crystalline salt.

By the action of acetic or formic acids on carbodiorthotolylimide, ditolylcarbamide is produced, together with acetic anhydride or carbonic oxide. It is suggested that the additive compound,

$$C(OAc)_2(C_7H_7\cdot NH)_2,$$
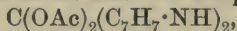
is formed as an intermediate product.

Phenylallylcarbamide, $C_3H_5\cdot NH\cdot CO\cdot NHPh$, melts at 113°, and not at 97° as stated by Maly (*Zeit. Chem.*, 1869, [ii], **5**, 258); it is also shown that the substance melting at 105° which was prepared by Bizio (*J. prakt. Chem.*, 1862, **86**, 292) by desulphurising phenylallylthiocarbamide is phenylallylcarbamide, and not carboallylphenylimide, as has usually been assumed. *Carboallylphenylimide*, $C_3H_5\cdot N\dot{:}C\dot{:}NPh$, was obtained as an oil which could not be purified owing to its instability; it gave, however, an unstable imidocarbamate by the action of alcohol and sodium ethoxide, formed a definite sesquichloride, and was decomposed in the normal way by formic acid, giving phenylallylcarbamide and carbonic oxide.

Unlike the imido-ethers, the imidocarbamates are very stable towards water; by the action of cold dilute hydrochloric acid, methylic orthotolylimidotolylcarbamate gives ditolylcarbamide, and a small amount of tritolylguanidine; ethylic phenylimidophenylcarbamate behaves in a similar manner. By the action of acetic acid, methylic orthotolylimidotolylcarbamate gives ditolylcarbamide and methylic acetate. Concentrated sulphuric acid acting on ethylic phenylimidophenylcarbamate gives aniline, alcohol, and carbonic anhydride, but no trace of phenylurethane. Unlike the imido-ethers, the imidocarbamates are only acted on with difficulty by ammonia, but on heating together at 200° the corresponding guanidine is produced. On heating ethylic phenylimidophenylcarbamate at 295—300°, ethylene is given off, and the residue contains carbanilide and polymerised carbodiphenylimide; it is therefore probable that the combination of alcohol with carbodiphenylimide is reversed at high temperatures. The imidocarbamates are not decomposed by boiling with potassium hydroxide, but at 160° methylic orthotolylimidotolylcarbamate is converted into toluidine, methylic alcohol, and carbonic anhydride. Ethylic phenylimidophenylcarbamate, when heated in a current of hydrogen sulphide at 190°, is converted into aniline, carbon bisulphide, and ethylic alcohol, together with a certain amount of diphenylcarbamide and mercaptan, and when heated with carbon disulphide at 170°, gives carbonyl sulphide, diphenylthiocarbamide, and phenylic thiocyanate, whilst methylic orthotolylimidotolylcarbamate gives ditolylthiocarbamide and tolylic thiocyanate on similar treatment; these two reactions are precisely similar to those which the amidines undergo when acted on by hydrogen sulphide and by carbon bisulphide respectively.

By the action of acetic chloride on ethylic phenylimidophenylcarbamate, diphenylcarbamide and acetodiphenylcarbamide are pro-

duced, whilst benzoic chloride gives diphenylcarbamide and *benzo-diphenylcarbamide*, NHPh·CO·NPh·COPh ; the latter is insoluble in water, but readily soluble in organic solvents, it crystallises in fine white needles, and melts at 131° ; when heated, it dissociates into benzanilide and phenylcarbimide.

The silver salt of dicarbethoxycarbamide, when acted on with ethylic iodide, gives *ethoxycarbonyldiurethane*,

$$\text{COOEt·NH·C(OEt)}{:}\text{N·COOEt} ;$$
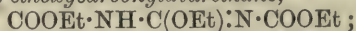
this is a colourless, mobile oil, insoluble in water and dilute alkalis, and cannot be distilled at ordinary pressures, as it is completely decomposed. Dry hydrogen chloride acts on it at 0°, giving dicarbethoxycarbamide and ethylic chloride, and a similar change takes place slowly in presence of cold dilute hydrochloric acid. Alcoholic ammonia converts it very readily into dicarbethoxyguanidine. The sodium salt of dicarbethoxycarbamide appears to give only nitrogen ethers when treated with ethylic iodide.

<div align="right">T. M. L.</div>

Preparation of Alkylisocarbamides from Cyanamides. By JULIUS STIEGLITZ and R. H. McKEE (*Ber.*, 1899, **32**, 1494—1496. Compare Abstr., 1894, i, 333, and Dains, preceding abstract).—When hydrogen chloride is led into an ice cold alcoholic solution of phenylcyanamide and the mixture left for two days, condensation occurs, and *ethylic imidophenylcarbamate (isophenylcarbamide)*, NHPh·C(OEt):NH, is formed, and is isolated by pouring into 15 per cent. potassium hydroxide, extracting with ether, and dissolving the residue in light petroleum (40—60°) ; when purified by distillation under reduced pressure, it forms a colourless oil distilling at 138·5° under 19 mm. pressure, and having a somewhat basic odour and a refractive index 1·5575 at 23° ; it is readily soluble in most organic solvents, sparingly in cold water, yielding a solution with a strongly alkaline reaction. When decomposed with dry hydrogen chloride, it yields ethylic chloride and phenylcarbamide. The *platinochloride*, $(C_9H_{12}N_2O)_2,H_2PtCl_6$, has a deep yellow colour, and is sparingly soluble in alcohol or water.

<div align="right">J. J. S.</div>

Conversion of Phenylcarbamine and Phenylthiocarbimide into Acetanilide. By BRONISLAW PAWLEWSKI (*Ber.*, 1899, **32**, 1425—1426).—It is well known that phenylcarbamine and acetic acid yield formanilide and acetic anhydride. Acetanilide is obtained, however, when phenylcarbamine is heated with thiacetic acid until the mixture begins to boil. Thiacetic acid also reacts more readily with phenylthiocarbimide than acetic acid does (Werner, Trans., 1891, 544) ; here also the main product, after boiling for half an hour, is acetanilide.

Dichloracetic acid reacts readily with phenylcarbamine, forming dichloracetanilide.

Some solubilities of acetanilide and of dichloracetanilide are given in the paper.

<div align="right">C. F. B.</div>

Action of Aniline on Dithioacetylacetone. By VICTOR VAILLANT (*Bull. Soc. Chim.*, 1898, **19**, [iii], 692—694. Compare Abstr., 1895, i, 168 ; 1896, i, 591 ; 1897, i, 265, and this vol., i, 415).—The

phenylimide of dithioacetylacetone, $S_2(CHAc \cdot CMe \vdots NPh)_2$, is produced when this substance is heated with aniline (2 mols.) at $100°$; the crystals which slowly separate from the product are washed with ether to remove resinous impurities, and then dissolved in alcohol. The phenylimide separates from this solvent in small, yellow crystals which darken above $120°$ and melt at $168°$. The *dihydrochloride*, $C_{22}H_{24}N_2S_2O_2,2HCl$, crystallises in white spangles when hydrogen chloride is passed into a chloroform solution of the phenylimide, and is also produced by the action of sulphur chloride on the phenylimide of acetylacetone dissolved in chloroform; it sublimes readily, and is soluble in water.

Benzidine readily condenses with dithioacetylacetone when molecular proportions of these substances are heated on the water bath; the condensation product which slowly separates from the mixture is washed with ether and crystallised from alcohol; analysis and a cryoscopic determination of the molecular weight indicate that the *compound* has the formula $C_{22}H_{22}N_2S_2O_2$; it separates from its solutions in alcohol and chloroform as a golden-yellow, crystalline powder, which darkens and decomposes above $150°$.   G. T. M.

ε-**Amidocaproic Acid.** By SIEGMUND GABRIEL and THEODOR A. MAASS (*Ber.*, 1899, **32**, 1266—1272).—δ-Phenoxybutylamine (Abstr., 1892, 131) was converted into δ-phenoxybutylphthalimide, then into δ-bromobutylphthalimide, this in its turn into ethylic phthalimidobutylmalonate, and finally into ε-amidocaproic acid.

δ-*Phenoxybutylbenzamide*, $OPh \cdot [CH_2]_4 \cdot NH \cdot COPh$, the benzoyl derivative of δ-phenoxybutylamine, crystallises from boiling light petroleum in glistening plates melting at $72°$.

δ-*Phenoxybutylphthalimide*, $OPh \cdot C_4H_8 \cdot N {\small{<}}^{CO}_{CO}{\small{>}} C_6H_4$, formed when phthalic anhydride and δ-phenoxybutylamine are heated together for some time at $200°$, crystallises in colourless rhombic plates melting at $101°$, and may be distilled under greatly reduced pressure without undergoing decomposition. δ-*Bromobutylphthalimide* is best obtained by shaking the phenoxy-compound for 2 hours at $100°$ with an aqueous solution of hydrogen bromide saturated at $0°$, and forms snow-white needles melting at $80·5°$. *Ethylic phthalimidobutylmalonate* $C_6H_4 {\small{<}}^{CO}_{CO}{\small{>}} N \cdot C_4H_8 \cdot CH(COOEt)_2$, is obtained as a colourless, thick oil when the bromo-compound is boiled for 2 hours with ethylic malonate, and a solution of sodium in absolute alcohol. When boiled with about four times its weight of hydrobromic acid of sp. gr. $1·49$ for 2—3 hours, it is converted into phthalic acid and *ε-amidocaproic acid hydrobromide*; this forms a fibrous, crystalline mass, which sinters at $90°$ and melts at $105°$. The *acid*, obtained by the action of moist silver oxide on the hydrobromide, forms a crystalline powder which sinters at $190°$ and melts at 202—$203°$. When carefully fused, gently heated until water is no longer given off, and then distilled under 10—15 mm. pressure, the lactam, $CH_2 {\small{<}}^{CH_2 \cdot CH_2 \cdot CO}_{CH_2 \cdot CH_2 \cdot NH}$, is obtained as an oil which solidifies to a mass of foliated crystals; it

is readily soluble in water, alcohol, ether, chloroform, or benzene, and crystallises from warm light petroleum in colourless plates melting at 65—69°, and consisting of the impure lactam. To purify the substance, it was converted into its aurichloride, $(C_6H_{11}NO)_2,HAuCl_4$, which crystallises from warm water in prisms melting at 75—76°. Pyrrolidone and phthalimidine form analogously constituted aurichlorides. Although amidocaproic acid has no poisonous properties, the lactam is a nerve poison.   J. J. S.

A New Series of Betaines. By AUGUST MICHAELIS and E. KÖHLER (*Ber.*, 1899, **32**, 1566—1572).—Monochloracetone and monobromacetophenone combine with triphenylphosphine, forming compounds of the type $PPh_3Cl \cdot CH_2 \cdot COMe$ and $PPh_3Br \cdot CH_2 \cdot COPh$ respectively, which differ very considerably from simple phosphonium compounds, since the halogen atom is readily replaced by hydroxyl by means of alkali carbonates. These hydroxy-compounds are not deliquescent and alkaline like the phosphonium hydroxides with which they are probably isomeric, but are neutral, crystalline, and almost insoluble in water. Probably they are to be regarded as phosphorbetaines, formed by the wandering of the hydrogen of the hydroxyl group attached to the phosphorus atom,

$$PPh_3{<}{\overset{CH_2 \cdot COMe}{OH}} \quad \rightarrow \quad PPh_3{<}{\overset{CH_2}{\underset{O}{-}}}{>}CMe \cdot OH.$$
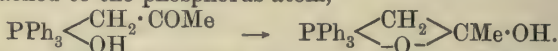
On treatment with halogen acids, they pass into the original halogen salt.

Triphenylmethylphosphorketobetaine, $PPh_3{<}{\overset{CH_2}{\underset{O}{-}}}{>}CMe \cdot OH$, is precipitated from an aqueous solution of its hydrochloride on the addition of sodium hydroxide, or aqueous sodium carbonate, as a white, flocculent precipitate; it crystallises in glistening needles, melts at 201°, and behaves towards solvents in the same way as Michaelis and von Gimborn's triphenylphosphorbetaine. The *hydrochloride*, $PPh_3Cl \cdot CH_2Ac$, is prepared by heating a molecular mixture of triphenylphosphine and monochloracetone on the water-bath for 45 minutes; it crystallises in slender needles which melt and partially decompose at 237°; the *platinochloride*, $(C_{21}H_{20}PO)_2PtCl_6$, crystallises in flesh-coloured leaflets melting and decomposing at 198°; the *hydrobromide* melts at 226°; the *picrate* forms lemon-yellow crystals and melts at 166°. *Tetraphenylphosphorketobetaine*, $PPh_3{<}{\overset{CH_2}{\underset{O}{-}}}{>}CPh \cdot OH$, formed in the same way from the hydrobromide, forms colourless crystals and melts at 183—184°; the *hydrobromide*, prepared from bromacetophenone and triphenylphosphine, melts at 273—274°, the *hydrochloride* crystallises in needles and melts at 254—255°, the *hydriodide* forms light, yellow needles and melts at 256—267°, and the *nitrate* forms colourless needles and melts at 184—185°.

Triphenylparatolylphosphorketobetaine,] $PPh_3{<}{\overset{CH_2}{\underset{O}{-}}}{>}C(C_7H_7) \cdot OH$,

prepared from the hydrochloride, crystallises in colourless, silky needles which melt at 181°. The *hydrochloride*, prepared from triphenylphosphine and chloroparatolyl methyl ketone, forms colourless needles melting at 231°, and is more soluble in water than the corresponding tetraphenyl derivative; the *platinochloride* forms reddish

yellow needles and melts and decomposes at 211°, the *hydrobromide* melts at 261°, the *hydriodide* at 265°, and the *nitrate* forms slender colourless crystals which melt at 183—184°. J. F. T.

Derivatives of Paratolualdehyde. By WENZEL HANZLIK and AL. BIANCHI (*Ber.*, 1899, **32**, 1285—1289).—Paratolualdehyde has a sp. gr. 1·072 at 12°, and a refractive index for sodium light 1·5484 at 14°; its sodium hydrogen sulphite compound consists of white, glistening plates readily soluble in water and sparingly soluble in alcohol or ether; its *phenylhydrazone* forms light yellow crystals melting at 108°, and the *parasulphophenylhydrazone* light yellow prisms melting at 270—271°.

Diparatoluylidenehydrazone (paratolylazine), $N_2(:CH·C_6H_4Me)_2$, prepared from the aldehyde and hydrazine, crystallises in lemon-yellow, rhombic prisms melting at 154—155°.

The compound of the aldehyde with *orthonitrophenylhydrazine* separates from dilute alcohol in red needles which melt at 181°, whilst the corresponding *paranitro*-derivative forms dark-red needles melting at 196°.

The *orthonitroparasulphophenylhydrazone* is an orange dye which is readily soluble in water and melts at 195°.

Paratoluylidenemetanitraniline forms brownish-yellow crystals melting at 79°, and the *para*-derivative crystallises from acetone in long, yellow needles melting at 135°.

Paratoluylidenemetanitrometaxylidine separates from its alcoholic solution in yellow, monoclinic plates melting at 145°, the corresponding *metanitroparaxylidine* forming light yellow prisms melting at 110°.

The *leuco-base* of *paramethylmalachite-green*, $C_6H_4Me·CH(C_6H_4·NMe_2)_2$, formed by the condensation of the aldehyde with excess of dimethylaniline in the presence of zinc chloride, crystallises in small needles which melt at 93—94°; its oxidation to the colour base, which closely resembles ordinary malachite-green in appearance and properties, is readily brought about by either chloranil in alcoholic solution, or by lead peroxide.

Metanitroparatolualdehyde is readily obtained by the nitration of paratolualdehyde, and crystallises from ether in long needles melting at 43—44°; the *phenylhydrazone* forms orange-coloured crystals melting at 112°; the *paranitrophenylhydrazone* is a reddish-brown, crystalline powder melting at 223—224°, and the *orthonitroparasulphophenylhydrazone* an orange wool-dye melting at 200—202°.

Dimetanitroparatoluylidenehydrazone is a light yellow, crystalline powder which melts at 184—185°, and *metanitroparatoluylidenemetanitraniline* separates from alcohol in light yellow needles melting at 156°. J. F. T.

Iodine Substitution Products of some Aromatic Alcohols, Aldehydes, and Acids. By JOHANNES SEIDEL (*J. pr. Chem.*, 1899, [ii], **59**, 105—149).—The main portion of this paper deals with the iodination of saligenin, salicylaldehyde, parahydroxybenzaldehyde, and anisaldehyde, which has previously been described (Abstr., 1898, i, 367, 663). Attempts have been made to iodinate coumarin directly, the best results being obtained by a modification of Kekulé and

Körner's methods (Kekulé, *Annalen*, 1864, **131**, 221; Körner, *ibid.*, 1866, **137**, 213). An alkaline solution of coumarin was saturated with carbonic anhydride, cooled, and the calculated quantity of iodine added; the product obtained was probably iodocoumaric acid, $OH \cdot C_6H_3I \cdot CH \vdots CH \cdot COOH$, a white powder melting at about 203°.

The results show that, contrary to Kekulé's theory, iodination can be effected in the case of substances having a pronounced phenolic character in the absence of an agent to combine with the hydrogen iodide formed; in other cases, however, the reaction must be carried out under pressure, and at a high temperature in the presence of iodic acid or a similar substance. F. H. N.

Elimination of Substituting Groups from the Benzene Ring. I. Behaviour of the Acyl and Carboxyl Groups. By AUGUST KLAGES and G. LICKROTH (*Ber.*, 1899, **32**, 1549—1565).—The formation of the double compounds of phosphoric acid with aromatic ketones described by Klages and Allendorff (Abstr., 1898, i, 477) is affected by the entrance of alkyl groups into the ring, depending however, not on the number or nature of such groups, but on the positions occupied by them. Thus these compounds are not formed when the ketone group is attached to the benzene ring in the ortho-position to two alkyl groups, acetylmesitylene not giving any compound, whilst acetylpseudocumene readily gives one. The behaviour of diacetylmetaxylene is interesting; this compound, which contains one acetyl group in the ortho-position to two alkyl groups and the other in the ortho-position to one, should combine with only one molecule of phosphoric acid, which, as a matter of fact, it does, whereas diacetyl-benzene combines with two mols. of the acid.

The behaviour of fatty aromatic ketones when boiled with phosphoric acid is also dependent on the position of the alkyl groups in the aromatic ring; compounds of the type $Ph \cdot CO \cdot R$, and compounds in which an alkyl group is substituted in the para- or meta-position to the acyl group remain unchanged, whilst when the alkyl group is in the ortho-position, about 20—30 per cent. of the compound is hydrolysed after boiling for 8 hours, and when the acyl group is in the ortho-position to two alkyl groups, complete hydrolysis ensues after heating for half an hour. This hydrolysis by means of phosphoric acid differs from that brought about by potassium hydroxide as disruption of the chain takes place, not between the alkyl group and the carbonyl, but between the carbonyl and the aromatic ring, forming a fatty acid and an aromatic hydrocarbon; thus, from diacetylmesitylene, diacetyldurene and diacetylisodurene, a quantitative yield of mesitylene, durene and isodurene respectively can be obtained. This action of phosphoric acid and the conditions which regulate it apply, not only to fatty aromatic ketones, but also to compounds in which the ketonic group is attached to radicles other than alkyl; thus mesitylenecarb-oxylic acid is quantitatively resolved into mesitylene and carbonic anhydride, durenecarboxylic acid behaving similarly, whilst prehnitene-carboxylic acid, under the same conditions, remains unchanged. In this reaction, hydrochloric acid, or, better still, hydriodic acid (b. p. 127°) may be substituted for phosphoric acid.

Ketones of the benzophenone group are only slowly hydrolysed by phosphoric acid. Thus benzoylmetaxylene yields 20 per cent. of the hydrocarbon after boiling for 8 hours and benzoylmesitylene and benzoyltriethylbenzene, 30 per cent. in the same time.

The phosphoric acid compound of acetophenone is decomposed in ethereal solution by aniline forming *aniline phosphate*, which crystallises from alcohol in glistening needles and melts at 180°. The *double compound* of arsenic acid and acetophenone crystallises from alcohol and melts sharply at 97°; it does not appear, however, to be a homogeneous substance.

Paracetyltoluene distils at 116° under 23 mm. and at 219° under ordinary pressure; its compound with phosphoric acid melts at 90°.

Paracetylethylbenzene boils at 130° under 23 mm. and at 236° under ordinary pressure, and has a sp. gr. 0·991 at 20°/4°; its phosphoric acid compound, which is deliquescent, melts at about 30°.

Parapropionylethylbenzene is a colourless, mobile liquid of intensely sweet taste, which boils at 246° and has a sp. gr. 0·986 at 18°/4°. The *oxime* forms large, rhombic plates and melts at 58—59°. The ethers of oxyketones also combine with phosphoric acid; thus the compound with *paracetylanisoil* melts at 86°, and that with paracetylphenetoil at 81°. Parapropionylanisoil does not combine with phosphoric acid, but on boiling with it is partially hydrolysed into anisoil. All these ketones were prepared from the aromatic hydrocarbons and the fatty acid chlorides by Friedel and Craft's reaction, but the following were prepared by Freund's method from the aromatic acid chloride and zinc methyl:

Metatoluic chloride is a colourless oil which distils at 120° under 38 mm. pressure and has a sp. gr. 1·173 at 20°/4°. *Metacetyltoluene* boils at 220° and has a sp. gr. 0·986 at 20°/4°.

Orthotoluic chloride boils at 100—102° under 21 mm. pressure, and with zinc methyl is converted into *orthacetyltoluene*, which boils at 213° (216° corr.) and has a sp. gr. 1·026 at 20°/4°.

Propionylpseudocumene, $C_6H_2Me_3 \cdot COEt$ [= 1 : 3 : 4 : 5], prepared from pseudocumene, propionic chloride, and aluminium chloride, boils at 154° under 29 mm., or at 257° under ordinary pressure, has a sp. gr. 0·985 at 18°/4°, and forms a compound with phosphoric acid which melts at 87°.

Propionylpentethylbenzene, prepared by Friedel and Craft's reaction, melts at 70—71° and boils at 179—180° under 19 mm. pressure.

Symmetrical trimethyldeoxybenzoin, $C_6H_2Me_3 \cdot CO \cdot CH_2Ph$, is at first obtained as a light yellow oil of sp. gr. 1·046 at 18°/4° which distils at 204° under 21 mm. pressure; it solidifies after some time and then forms colourless needles melting below 30°.

Triethylbenzophenone is a yellow oil of sp. gr. 1·032 at 20°/4° which boils at 210—220° under 40 mm. or at 340° under ordinary pressure. J. F. T.

Action of Sulphur Chloride on the Copper Derivative of Benzoylacetone. By VICTOR VAILLANT (*Bull. Soc. Chim.*, 1898, [iii], 19, 833—837).—It was shown in a previous paper (Abstr., 1895, i, 168) that the copper derivative of benzoylacetone reacts with

sulphur chloride in chloroform solution to form dithiobenzoylacetone, $S_2(CHAcBz)_2$; this substance, which has now been obtained in considerable quantity, forms pale yellow, rhombic crystals, has a slight aromatic odour, is optically active, melts at 117—118°, is insoluble in water, but more or less soluble in organic solvents, and gives a reddish-violet coloration with ferric chloride. The *sodium* derivative, $C_{20}H_{16}Na_2S_2O_4$, obtained by the action of sodium or, more readily, of sodium ethoxide on dithiobenzoylacetone in ethereal solution, is a yellow, crystalline compound which is very soluble in water, less soluble in alcohol, and insoluble in ether. The *copper* derivative, $C_{20}H_{16}CuS_2O_4$, obtained as a dark green, amorphous powder when an ethereal solution of dithiobenzoylacetone is added to a dilute alcoholic solution of cupric acetate, is insoluble in water, but soluble in ether or chloroform, and soon turns brown and decomposes at the ordinary temperature. The *ferric* derivative, $Fe_2(C_{20}H_{16}S_2O_4)_3$, obtained from the sodium compound by double decomposition, is a brick-red, amorphous powder, insoluble in water, slightly soluble in alcohol, and more soluble in chloroform. A canary-yellow, crystalline *compound* of the composition $C_{20}H_{18}S_2O_4,2NH_3$ is produced when a current of dry ammonia gas is passed into an ethereal solution of dithiobenzoylacetone, or when the latter is mixed with a saturated alcoholic solution of ammonia. It is very soluble in water, fairly soluble in alcohol, and rapidly decomposes on exposure to air, with evolution of ammonia. This decomposition is immediately brought about by dilute acids.

N. L.

Synthesis of Di-substituted Acetic Acids by means of Chloral. By PAUL FRITSCH and FELIX FELDMANN (*Annalen*, 1899, **306**, 72—86. Compare Abstr., 1898, i, 63).—The products of condensing chloral with benzene, toluene, and anisoil have been already described. *Diphenetyltrichlorethane*, $CCl_3 \cdot CH(C_6H_4 \cdot OEt)_2$, prepared by adding concentrated sulphuric acid to a solution of phenetoil and chloral hydrate in glacial acetic acid, crystallises in lustrous prisms, and melts at 105°.

Alcoholic potash converts derivatives of trichlorethane into the corresponding dichlorethylenes; diphenyldichlorethylene and ditolyldichlorethylene have been already described. *Dianisyldichlorethylene*, $CCl_2:C(C_6H_4 \cdot OMe)_2$, crystallises in stout, prismatic needles and melts at 113°; *diphenetyldichlorethylene*, $CCl_2:C(C_6H_4 \cdot OEt)_2$, melts at 106·5°.

When heated with alcoholic sodium ethoxide in sealed tubes at 180°, the dichlorethylene derivatives yield di-substituted acetic acids, associated in the case of ditolyldichlorethylene and diphenetyldichlorethylene with dimethyltolane and diethoxytolane respectively. *Ditolylacetic acid*, $COOH \cdot CH(C_6H_4Me)_2$, crystallises from glacial acetic acid in needles and melts at 144°. The *methylic* and *ethylic* salts melt at 36—37° and 65° respectively, whilst the *ammonium* salt crystallises in slender needles and rapidly loses ammonia at 100°; the *barium* and *calcium* salts contain $2H_2O$.

Dianisylacetic acid, $COOH \cdot CH(C_6H_4 \cdot OMe)_2$, forms lustrous needles melting at 110°. The *methylic* salt crystallises in lustrous plates and melts at 66—67°; the *barium* and *calcium* salts

crystallise in small needles containing $2H_2O$. *Diphenetylacetic acid,* $COOH \cdot CH(C_6H_4 \cdot OEt)_2$, melts at 114°; the *methylic* and *ethylic* salts melt at 68° and 47° respectively, whilst the *barium* and *calcium* salts crystallise in small needles containing $2H_2O$.

The constitution of the di-substituted acetic acids has been established by oxidising them to the corresponding ketones. M. O. F.

Condensation of Phenylisocrotonic Acid with Pyrocinchonic Anhydride. By JOHANNES THIELE (*Annalen*, 1899, **306**, 240—246).—*Cinnamylidenedimethylcrotonolactone (7-phenyl-2 : 3-dimethylheptatrieneolide-1 : 4),*

$$\begin{matrix} CMe\text{:}CMe \\ | \quad\quad\quad \\ CO\text{——}O \end{matrix}\Big> C\text{:}CH \cdot CH\text{:}CHPh,$$

prepared by heating sodium phenylisocrotonate with pyrocinchonic anhydride at 150° and treating the product with acetic anhydride, crystallises from alcohol in small, yellow needles and melts at 153°; the solution in concentrated sulphuric acid is orange-red, and alcoholic potash develops a yellow coloration which becomes dark brown on exposure to air. An alkaline solution of the lactone forms an intense red liquid with diazobenzenesulphonic acid or with diazobenzene, as in the case of a phenol.

Cinnamylidenedimethylcrotonolactonecarboxylic acid,

$$\begin{matrix} CMe\text{:}CMe \\ | \quad\quad\quad \\ CO\text{——}O \end{matrix}\Big> C\text{:}C(COOH) \cdot CH\text{:}CHPh,$$
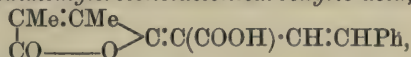
the initial product of condensing phenylisocrotonic acid with pyrocinchonic anhydride, crystallises from alcohol in small, yellow needles, and melts at 216°.

When cinnamylidenedimethylcrotonolactone is heated with alcoholic ammonia at 125—130° during 4 hours, the additive *compound,* $C_{15}H_{17}NO_2$, is obtained, crystallising in white leaflets containing $1H_2O$ and melting at 113°; the anhydrous substance melts at 142°. Mineral acids convert it into the *imide,* $C_{15}H_{15}NO$, which consequently forms the chief product of the action of alcoholic ammonia on cinnamylidenedimethylcrotonolactone; it crystallises from glacial acetic acid in small, yellow needles, and melts indefinitely at 248°.

M. O. F.

Formation of a Hydroxylactone by the Condensation of Benzaldehyde and Pyruvic Acid. By EMIL ERLENMEYER, jun., (*Ber.*, 1899, **32**, 1450—1455. Compare Abstr., 1894, i, 592).—The condensation of benzaldehyde and pyruvic acid has already been studied by Claisen and Claparède (Abstr., 1882, 520), who obtained as chief product cinnamylformic acid; working under exactly the same conditions, the author has obtained, in addition, two crystalline derivatives. One of these, *γ-phenyl-β-benzylidene-α-ketobutyrolactone,*

$$CO\begin{matrix}O\text{——}CHPh \\ \\ CO \cdot C\text{:}CHPh\end{matrix},$$

is formed in only minute quantities under the conditions employed by Claisen and Claparède, but a good yield may be obtained by saturating a mixture of benzaldehyde (2 mols.) and pyruvic acid (1 mol.) at low temperatures with dry hydrogen chloride and keeping the mixture for 3 days at the ordinary temperature, then extracting with water, and precipitating from the aqueous solution with ether; it

crystallises in well-defined, yellow prisms melting at 167°, and combines with bromine yielding a *dibromide* which crystallises in colourless needles melting at 135°, but another product melting at 209° is also formed, and part of the lactone remains unchanged. The lactone has neutral properties, but dissolves in alkalis, yielding salts of *γ-hydroxy-γ-phenyl-β-benzylidene-α-ketobutyric acid*,

$$OH \cdot CHPh \cdot C(:CHPh) \cdot CO \cdot COOH.$$
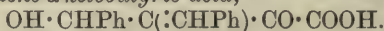
The *sodium* salt, with $4H_2O$, crystallises in colourless, flat needles; the *barium* and *silver* salts were also prepared. When the lactone is warmed with sodium hydroxide solution, benzaldehyde is formed, and when oxidised with dilute nitric acid, benzoic acid is the chief product; with alkaline permanganate, oxalic acid is formed.　　　J. J. S.

Ethylic Trinitrophenylmalonate. By C. LORING JACKSON and J. I. PHINNEY (*Amer. Chem. J.*, 1899, **21**, 418—433).—Ethylic trinitrophenylmalonate, which was originally obtained in long, white, slender plates melting at 58° (Abstr., 1896, i, 234, 370), has been obtained in a new form by acidifying a solution of the ammonium salt; it then crystallises in four (or six)-sided plates, in which two opposite angles are unlike, one being acute and the other obtuse, and melts at 64°. Since the discovery of this form, it has always been obtained to the entire exclusion of the other, and even when specimens of the first modification have been recrystallised, they have undergone conversion into the second; this behaviour is doubtless due to the dissemination of particles of the stable modification through the building in which the experiments have been conducted, as it is found that the minutest trace is sufficient to convert the form of low melting point in saturated solution into that of high melting point.

It is believed that the difference between the two forms is due to the same cause as that existing between the two forms of ethylic anilidotrinitrophenyltartronate (Jackson and Bentley, Abstr., 1892, 1217), and that the difference is of a chemical, and not of a purely physical, nature appears certain from the fact that both have been converted into salts and recovered unchanged on acidification. It is suggested that possibly one contains the enolic and the other the ketonic form of the malonic residue. The new modification is white, but gives dark-red salts; the *ammonium* salt is composed of rich golden-brown, hair-like needles, decomposes below 100°, and afterwards melts to a yellowish-brown liquid, which explodes at higher temperatures. An aqueous solution of the ammonium salt gives red precipitates with salts of strontium, calcium, zinc, cadmium, copper, and lead, and a crystalline, amethyst-coloured precipitate with barium salts.

When nitric acid acts on ethylic trinitrophenylmalonate, the *nitrite*, $C_6H_2(NO_2)_3 \cdot C(COOEt)_2 \cdot O \cdot NO$, of the corresponding ethylic trinitrophenyltartronate is obtained, which crystallises in long, flat, white prisms, belonging apparently to the monoclinic system, melts and decomposes at 109°, dissolves readily in ethylic and methylic alcohols, chloroform, ether, benzene, acetic acid, or acetone, is nearly insoluble in carbon bisulphide and in cold water, but dissolves sparingly in hot water, giving a pink solution. Cold mineral acids

have no effect on the substance, which is decomposed by hot sulphuric acid, however, and is converted into the corresponding ethylic tartronate by hot nitric acid ; it is gradually dissolved by alkalis, giving red solutions.

Ethylic trinitrophenyltartronate, $C_6H_2(NO_2)_3 \cdot C(COOEt)_2 \cdot OH$, forms aggregates of white, fluffy needles, melts at 117°, dissolves readily in ethylic and methylic alcohols, ether, benzene, chloroform, or acetone, is soluble in glacial acetic acid, somewhat soluble in carbon bisulphide, and sparingly so in light petroleum. It is decomposed by hot sulphuric acid, gas being evolved, and appears to be hydrolysed by alkalis. The *acetyl* derivative forms white, flat, probably monoclinic prisms. The *benzoyl* derivative forms white crystals melting at 152°.

Trinitrophenylacetic acid, $C_6H_2(NO_2)_3 \cdot CH_2 \cdot COOH$, made by boiling ethylic trinitrophenylmalonate with sulphuric acid of sp. gr. 1·44 for some hours, crystallises from benzene in short needles melting at 161°; it is converted into the corresponding trinitrotoluene (m. p. 81°) when warmed with alcohol or water. It dissolves readily in ether, glacial acetic acid, acetone, or light petroleum, is soluble in chloroform, and less so in benzene or carbon bisulphide.

Attempts to prepare ethylic ditrinitrophenylmalonate have proved unsuccessful. A. L.

Addition of Hydrogen Cyanide to Ethylic Cinnamylidene-malonate. By JOHANNES THIELE and JAKOB MEISENHEIMER (*Annalen*, 1899, **306**, 247—266. Compare Bredt and Kallen, Abstr., 1897, i, 154).—Cinnamylidenemalonic acid has been described by Liebermann (Abstr., 1895, i, 470) ; the *methylic* and *ethylic* salts melt at 67° and 36°, respectively.

Cinnamenylsuccinic acid, $CHPh{:}CH \cdot CH(COOH) \cdot CH_2 \cdot COOH$, prepared by heating an alcoholic solution of ethylic cinnamylidenemalonate with potassium cyanide and hydrolysing the nitrile with 5 per cent. caustic potash, separates from dilute alcohol in prismatic crystals and melts at 173°. The *anhydride* melts at 116°.

Benzylparaconic acid, $CO{<}^{CH_2 \cdot CH \cdot COOH}_{O\underline{}CH \cdot CH_2Ph}$, obtained from cinna-menylsuccinic acid by the action of hydrogen bromide in glacial acetic acid, crystallises in white prisms and melts at 93°.

Phenethylsuccinic acid, $CH_2Ph \cdot CH_2 \cdot CH(COOH) \cdot CH_2 \cdot COOH$, prepared by heating cinnamenylsuccinic acid with hydriodic acid and red phosphorus, is also produced by hydrolysing the nitrile from ethylic phenylpropylidenemalonate (see below) and hydrogen cyanide ; it crystallises from benzene and melts at 136°. The *anhydride* melts at 56° ; the *paratolilic acid* crystallises in colourless needles melting at 146° and yields the *hydrogen ammonium* salt in leaflets which melt and evolve gas at 185°.

Phenylpropenylmalonic (1 : 4-*hydrocinnamylidenemalonic*) *acid*, $CH_2Ph \cdot CH{:}CH \cdot CH(COOH)_2$, formed when cinnamylidenemalonic acid is reduced in alkaline solution with sodium amalgam, crystallises from benzene in white leaflets which melt and decompose at 106—108° ; the *sodium* salt is anhydrous, and the *barium* salt contains $1H_2O$.

Phenylpropylidenemalonic (3 : 4-*hydrocinnamylidenemalonic*) *acid*,

$CH_2Ph \cdot CH_2 \cdot CH:C(COOH)_2$, obtained from the foregoing acid by pro-
tracted treatment with caustic soda on the water-bath, melts and
decomposes at 115—116°; the *barium* salt contains $1H_2O$.

Phenylbutanetricarboxylic acid, $C_4H_6Ph(COOH)_3$, prepared by hydro-
lysing the nitrile from ethylic cinnamylidenemalonate and potassium
cyanide, melts indefinitely at 180—185°; the *methylic* salt crystallises
in large prisms melting at 46°, and boils at 328—336° under 718 mm.
pressure. The *anhydride* crystallises from benzene in leaflets and
melts at 112°.   M. O. F.

Action of Sulphuric Acid on Thymol. By JAMES H. STEBBINS
(*J. Amer. Chem. Soc.*, 1899, **21**, 276—281. Compare *ibid.*, 1881, **3**,
103—110).—The chief product of the sulphonation of thymol with
sulphuric acid of sp. gr. 1·83 at 100° is the para-acid [Me:SO_3H:Pr:OH
$= 1 : 2 : 4 : 5$]; its constitution has been established by Claus (Abstr.,
1899, 899), and is also shown by the formation of the thymoquinone
melting at 45·5° when oxidised with chromic acid. The ortho-acid
[Me:SO_3H:C_3H_7:OH $= 1 : 2 : 4 : 3$] does not appear to be produced, but
a small quantity of a disulphonic acid was separated.   T. M. L.

Disulphones. I. Nitrogen Derivatives of Sulphonal. By
THEODOR POSNER (*Ber.*, 1899, **32**, 1239—1251).—Gabriel and Posner
(Abstr., 1894, i, 355) have shown that amidoacetone-ethylmercaptole
cannot be obtained by the action of hydrochloric acid on phthalimido-
acetone-ethylmercaptole, as the reaction proceeds further and phthalic
acid, ethylmercaptan, and amidoacetone hydrochloride are the final
products. Amidosulphonal may, however, be prepared by a different
method. *Phthalimidosulphonal* (*phthalimidoacetonediethyldisulphone*),

$C_6H_4{<}^{CO}_{CO}{>}N \cdot CH_2 \cdot CMe(SO_2Et)_2$, is obtained when phthalimidoacetone-

ethylmercaptole is carefully dissolved in cold acetic acid and then
oxidised with an excess of a cold saturated solution of potassium
permanganate; it forms large, lustrous, colourless plates, melts at
175—177° (corr.), is practically insoluble in water, but dissolves readily
in alcohol or acetic acid.

When treated with strong potassium hydroxide solution, a heavy
oil consisting of *potassium sulphonalphthalamate* is formed, which is
readily soluble in water, and when warmed with hydrochloric acid yields
sulphonalphthalamic acid, $CMe(SO_2Et)_2 \cdot CH_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot COOH$,
which, when boiled with concentrated hydrochloric acid, is hydrolysed
to phthalic acid and *amidosulphonal hydrochloride*; a better yield of the
latter is obtained when phthalimidosulphonal is heated for 3 hours at
170° with concentrated hydrochloric acid; the *base* itself,

$$NH_2 \cdot CH_2 \cdot CMe(SO_2Et)_2,$$
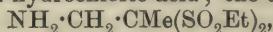
may be obtained by treatment with an excess of alkali and repeated
extraction with ether; it crystallises in short, monoclinic prisms melt-
ing at 94—96° (corr.), is moderately soluble in cold, readily in hot
water and also in most organic solvents with the exception of light
petroleum. The *hydrochloride* crystallises from alcohol in small,
colourless needles, or in well-developed, rhombic plates melting at
190—191° (corr.); the *platinochloride* crystallises in orange-yellow

prisms ·melting and decomposing at 225°, the *picrate* is sparingly soluble in water, but the *sulphate, nitrate,* and *oxalate* are readily soluble. When a hydrochloric acid solution of the base is treated with sodium nitrite, a small quantity of a substance melting at 71—75° is obtained ; whether this is hydroxysulphonal has not been determined.

Nitrosoacetone-ethylmercaptole, $NO \cdot CH_2 \cdot CMe(SEt)_2$, is obtained when an ethereal solution of isonitrosoacetone and ethylmercaptan is saturated in the cold with dry hydrogen chloride and left until the ether has evaporated ; it is a yellowish-red oil, and is so readily decomposed that it cannot be purified. When the chloroform solution is mixed with acetic acid and oxidised with an excess of potassium permanganate, *nitrososulphonal,* $NO \cdot CH_2 \cdot CMe(SO_2Et)_2$ is obtained, which crystallises from alcohol in well-developed, six-sided rhombic plates melting at 104—105° (corr.).

Isonitrosomethylacetone (Ceresole, *Ber.,* 1883, **16,** 833) also condenses with mercaptan in the presence of hydrogen chloride, and the product when oxidised gives *methoxyamidopropane-αββ-triethylsulphone* (*isonitrosomethylacetonetriethylsulphone*),

$$OMe \cdot NH \cdot CH(SO_2Et) \cdot CMe(SO_2Et)_2,$$
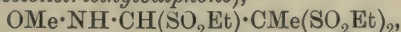
and is therefore probably methoxyamido-αββ-trithioethylpropane, $OMe \cdot NH \cdot CH(SEt) \cdot CMe(SEt)_2$, formed by the direct union of ethylmercaptan with isonitrosomethylacetone-ethylmercaptole ; the trisulphone crystallises in colourless plates and melts at 72° (corr.). Ethylisonitrosoacetone, boiling at 130°, when treated in a similar manner, yields a reddish oil which, on oxidation, gives *isonitrosoethylacetonetriethyltrisulphone,* $OEt \cdot NH \cdot CH(SO_2Et)CMe(SO_2Et)_2$; it crystallises in long, colourless prisms, is readily soluble in hot ethylic acetate or alcohol, and is very stable, being only partially decomposed when heated for 2 hours at 200° with concentrated hydrochloric acid. The yields of isonitrosoethylacetone and of its trisulphone derivative are much better than in the case of the methylic compounds.

Ethylic nitrosoacetoacetate also condenses with ethylmercaptan, but the product, when oxidised, does not yield a crystalline sulphone.

The condensation of diphthalimidoacetone (Abstr., 1894, i, 355) with mercaptan does not take place at all readily, on account of the slight solubility of the acetone derivative in most solvents ; it is most easily effected by using an acetic acid solution saturated in the cold with hydrogen chloride, and heating with the mercaptan for several hours in sealed tubes at 60—70° ; the *diphthalimidacetone-ethylmercaptole,* $C(SEt)_2 \left(C_6H_4 {<}^{CO}_{CO}{>} N \cdot CH_2 \right)_2$, is precipitated by the addition of water, and forms a white powder melting at 176—177° ; when oxidised, it yields *diphthalimidosulphonal,*

$$C(SO_2Et)_2 \left(C_6H_4 {<}^{CO}_{CO}{>} N \cdot CH_2 \right)_2,$$
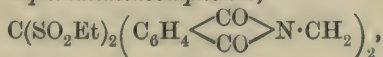
melting at 218—220°.

The product obtained by Hörmann (Abstr., 1881, 248) by oxidising symmetrical dichlorhydrin is not dichloracetone but pseudodichloracetone, since, when heated with potassium phthalimide, it does not

yield diphthalimidoacetone melting at 268°, but an isomeric compound melting at 220°, to which the constitution

$$C_6H_4{<}^{CO}_{CO}{>}N{\cdot}CH_2{\cdot}\overset{O}{\overset{\diagup\diagdown}{CH{-}CH}}{\cdot}N{<}^{CO}_{CO}{>}C_6H_4$$
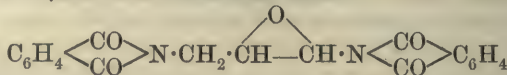
is ascribed.　　　　　　　　　　　　　　　　　　　　　　　　J. J. S.

Iodoso- and Iodoxy-compounds of Di-iododiphenylsulphone. By CONRAD WILLGERODT and O. WALDEYER (*J. pr. Chem.*, 1899, [ii], **59**, 194—197. Compare Langmuir (Abstr., 1895, i, 230).—*Iodiodoso-diphenylsulphone*, $C_6H_4I{\cdot}SO_2{\cdot}C_6H_4{\cdot}IO$, a bright yellow, amorphous powder decomposing at 184°, was obtained from di-iododiphenyl-sulphone by converting it into iododiphenyl iodochloride by means of chlorine, and treating this with dilute sodium hydroxide.

Di-iodoxydiphenylsulphone, $SO_2(C_6H_4{\cdot}IO_2)_2$, was obtained as a very sparingly soluble, colourless substance exploding at 212° by oxidising the iodiodoso-compound with hypochlorous acid.

Attempts to prepare pariodosobenzenesulphonic acid were unsuccessful.　　　　　　　　　　　　　　　　　　　　　　　　F. H. N.

Sulphonated Butyric Acids. By JULIUS TROEGER and ROBERT UHDE (*J. pr. Chem.*, 1899, [ii], **59**, 320—349. Compare Otto (Abstr., 1890, 379, &c.)—*Ethylic phenylsulphonebutyrate*, $SO_2Ph{\cdot}CHEt{\cdot}COOEt$, made by heating sodium benzenesulphinate and ethylic a-bromo-butyrate in alcoholic solution for 30 hours on the water-bath, crys-tallises from alcohol in shining, prismatic forms melting at 60—61°, and is soluble in alcohol, ether, and acetic acid, but insoluble in water. The acid, $SO_2Ph{\cdot}CHEt{\cdot}COOH$, which has already been obtained in small quantity by Otto (*loc. cit.*), dissolves in alcohol, ether, acetic acid, or hot water, and melts at 123—124°. The *sodium* salt cannot be dried on the water-bath, and loses carbonic anhydride at 110°. The *barium* salt, $(C_{10}H_{11}SO_4)_2Ba$, and the *calcium* salt, $(C_{10}H_{11}SO_4)_2Ca$, form glassy masses. The *silver* salt, $(C_{10}H_{11}SO_4Ag)$, crystallises in fine leaflets from hot water.

Ethylic paratolylsulphonebutyrate, $C_7H_7{\cdot}SO_2{\cdot}CHEt{\cdot}COOEt$, crys-tallises in slender needles, melts at 42°, and is insoluble in water, but dissolves in alcohol, ether, acetic acid, or ethylic acetate. The *acid* sinters at 42° and melts at 47°. The *sodium* salt, $(C_{11}H_{13}SO_4Na)$, is a syrupy mass which cannot be dried. The *barium* salt, $(C_{11}H_{13}SO_4)_2Ba + H_2O$, forms microscopic needles. The *silver* salt, $C_{11}H_{13}SO_4Ag$, forms small leaflets.

Ethylic a-naphthylsulphonebutyrate, $C_{10}H_7{\cdot}SO_2{\cdot}CHEt{\cdot}COOEt$, crys-tallises in shining, granular crystals which melt at 71—72°. The *acid* forms a crystalline powder, melts at 82°, and dissolves in alcohol, ether, acetic acid, and ethylic acetate, but is only sparingly soluble in hot water. The *sodium* salt is syrupy. The *barium* salt, $(C_{14}H_{13}SO_4)_2Ba + 3H_2O$, forms crystals which readily effloresce.

Ethylic β-naphthylsulphonebutyrate, $C_{16}H_{18}SO_4$, crystallises from dilute alcohol in slender needles and melts at 63—64°. The *acid*, $C_{14}H_{14}SO_4 + H_2O$, crystallises from dilute alcohol in slender, white needles

melting at 110°, and dissolves in alcohol, ether, acetic acid, ethylic acetate, and much hot water. The *sodium* salt is syrupy. The *barium* salt, $(C_{14}H_{13}SO_4)_2Ba + 3H_2O$, forms microscopic prisms.

Ethylic phenylsulphonisobutyrate, $SO_2Ph \cdot CMe_2 \cdot COOEt$, forms white crystals and melts at 38—39°. The *acid* is much more difficult to prepare by the hydrolysis of the ethylic salt than is the corresponding normal acid. The *sodium* salt, $C_{10}H_{11}SO_4Na + 3H_2O$, separates from hot aqueous solution in slender, transparent needles. The *barium* salt, $(C_{10}H_{11}SO_4)_2Ba$, forms fine, white leaflets.

Ethylic paratolylsulphonisobutyrate, $C_7H_7 \cdot SO_2 \cdot CMe_2 \cdot COOEt$, forms light yellow crystals and melts at 79—80°. The *acid* forms white crystals, melts at 124—125°, and is soluble in alcohol, ether, ethylic acetate, or hot water. The *sodium* salt, $C_{11}H_{13}SO_4Na$, crystallises in microscopic prisms. The *barium* salt, $(C_{11}H_{13}SO_4)_2Ba$, crystallises in slender, felted needles.

Ethylic a-naphthylsulphonisobutyrate, $C_{10}H_7 \cdot SO_2 \cdot CMe_2 \cdot COOEt$, melts at 90°. The *acid* forms a white, crystalline powder and melts at 183—184°. The *sodium* salt, $C_{14}H_{13}SO_4Na$, was obtained in crystalline crusts; the *barium* salt, $(C_{14}H_{13}SO_4)_2Ba$, in microscopic, slender needles.

Ethylic β-naphthylsulphonisobutyrate, $C_{10}H_7 \cdot SO_2 \cdot CMe_2 \cdot COOEt$, is obtained in yellowish-green crystals which melt at 63—64°. The *acid* forms white, rhombic crystals melting at 170°. The *sodium* salt, $C_{14}H_{13}SO_4Na$, is obscurely crystalline; the *barium* salt crystallises in slender, white needles.

When the sodium salt of phenylsulphonebutyric acid is heated, it loses carbonic anhydride, and Otto's normal phenylpropylsulphone is produced. A similar reaction occurs when the corresponding tolyl-sulphone acid is heated.

a-Naphthylpropylsulphone, $C_3H_7 \cdot SO_2 \cdot C_{10}H_7$, is made by heating the sodium salt of the corresponding carboxylic acid at 115°; it forms elongated prisms, melts at 67—68°, and dissolves in alcohol, ether, acetic acid, benzene, or light petroleum, but is insoluble in water.

β-Naphthylpropylsulphone, $C_{13}H_{14}SO_2$, crystallises in white, felted needles melting at 73°.

In order to induce a similar decomposition of the corresponding derivatives of isobutyric acid, it is necessary to heat them with free alkali in closed tubes at 170°. The sodium salt of phenylsulphon isobutyric acid, when treated in this way, yields *phenylisopropylsulphone*.

Paratolylisopropylsulphone, $CHMe_2 \cdot SO_2 \cdot C_7H_7$, crystallises in prisms and melts at 80°.

a-Naphthylisopropylsulphone, $CHMe_2 \cdot SO_2 \cdot C_{10}H_7$ forms light yellow, prismatic crystals melting at 52°.

β-Naphthylisopropylsulphone forms crystals melting at 73°.

Otto has shown that the sulphonated acetic acid is attacked by halogens without separation of the sulphone group, and that an atom of halogen may be introduced into sulphonated propionic acid, but that the products are so unstable that on boiling they break up into carbonic anhydride and a substituted sulphone. The authors have extended these observations with the following results.

When phenylsulphonebutyric acid is warmed on the water-bath with

bromine and water, the colour disappears, and the product, on fractional crystallisation, may be separated into two substances, one neutral and the other acid. The neutral product is *phenylbromopropylsulphone*, $CH_2Me \cdot CHBr \cdot SO_2Ph$; this crystallises in white, feathery needles and melts at 77—78°; the acid substance is *phenylsulphonebromobutyric acid*, $C_{10}H_{11}BrSO_4$, which may be obtained free from the neutral product by conducting the treatment with bromine in sealed tubes at 100° in absence of water; it dissolves in alcohol, ether, acetic acid, or benzene, forms a crystalline powder melting at 114—115°, and when boiled with water breaks up into carbonic anhydride and bromo-propylsulphone.

Paratolylsulphonebromobutyric acid, $C_{11}H_{13}BrSO_4$, melts at 78—79°. *Paratolylmonobromopropylsulphone*, $CHBrEt \cdot SO_2 \cdot C_7H_7$, forms glassy crystals melting at 93—94°.

When α-naphthylsulphonebutyric acid is heated with bromine at 100°, a *dibromo*-acid, $C_{14}H_{12}Br_2SO_4$, is obtained which melts and decomposes at 190°. It is probable that in this substance the second bromine atom is in the naphthalene nucleus.

A *dibromo-β-naphthylsulphonebutyric acid*, $C_{14}H_{12}Br_2SO_4$, is formed when β-naphthylsulphonebutyric acid is heated with bromine; it melts and decomposes at about 148°.

Phenylsulphonisobutyric acid does not yield a definite product when treated with bromine, but the corresponding paratolyl acid yields a *monobromo*-acid, possibly $CH_2Br \cdot C_6H_4 \cdot SO_2 \cdot CMe_2 \cdot COOH$, which melts at 103—104°.

α-Naphthylsulphonisobutyric acid, on treatment with bromine, yields a *dibromo*-acid, possibly $C_{10}H_5Br_2 \cdot SO_2 \cdot CMe_2 \cdot COOH$, which forms bright yellow leaflets and melts at 187°. A *dibromo*-acid is also obtained from the β-naphthyl compound, and forms yellow leaflets melting at 195°. Neither of the foregoing acids is decomposed when the sodium salt is boiled with water.

The ethylic salts of the sulphonated butyric acids may be brominated at the temperature of the water-bath. *Ethylic phenylsulphonebromobutyrate* was obtained in a crystalline form and gave the corresponding acid on hydrolysis. The bromination of ethylic paratolylsulphonebutyrate gave only ethylic bromide and the monobromo-acid already described; similar results were obtained with the other ethylic salts. Ethylic phenylsulphonisobutyrate gave phenylsulphonisobutyric acid only.

The chlorides of sulphonated butyric acids, unlike those of the corresponding acetic acids, are, as a rule, easily prepared by the action of phosphorus pentachloride on the acid at ordinary or slightly elevated temperatures.

Phenylsulphonebutyric chloride forms crystals which melt at 48°. *Paratolylsulphonebutyric chloride* was obtained in the form of an oil which, on treatment with alcohol, gave the corresponding ethylic salt. *α-Naphthylsulphonebutyric chloride* crystallises in slender, aggregated needles which melt at 81—82°. *β-Naphthylsulphonebutyric chloride* crystallises in nodular aggregates of needles and melts at 77—78°.

Phenylsulphonisobutyric chloride forms crystals melting at 37°. *Paratolylsulphonisobutyric chloride* melts at 38—42°. *α-Naphthyl-*

sulphonisobutyric chloride separates from light petroleum in small, rhombic tablets and melts at 75—76°. *β-Naphthylsulphonisobutyric chloride* crystallises in nodular aggregates of needles and melts at 76°.

<div align="right">A. L.</div>

Reduction of Benzil. By JOHANNES THIELE (*Annalen*, 1899, 306, 142—145).—The formation of *stilbenediol*, OH·CPh:CPh·OH, as an intermediate product in the reduction of benzil to benzoin, is established by conducting the experiment in presence of concentrated sulphuric acid and acetic anhydride, when the latter arrests the dihydroxy-compound in the form of acetyl derivatives.

The *a-diacetyl* derivative of stilbenediol crystallises from benzene in small, white needles and melts at 153°; it dissolves less readily in common solvents than the *β-acetyl* derivative, which melts at 110°. Both modifications decolorise an alkaline solution of potassium permanganate, but do not combine readily with ammonia; alcoholic potash converts them into benzoin.

<div align="right">M. O. F.</div>

Dibenzylidenepropionic Acid and Phenacylcinnamic Acid. By JOHANNES THIELE (*Annalen*, 1899, 306, 145—171).—*Dibenzylidenepropionic acid*, CHPh:CH·C(:CHPh)·COOH, prepared by heating dried sodium phenylisocrotonate with acetic anhydride and benzaldehyde at 140° during 20—25 minutes, crystallises from alcohol in pale yellow needles and melts at 167°, diphenylbutadiene (compare Rebuffat, Abstr., 1885, 1137), arising from elimination of carbonic anhydride, being also produced. The *barium*, *calcium*, and *silver* salts are anhydrous; the *methylic* salt is a viscous, brownish-yellow oil. *Meta-nitrodibenzylidenepropionic acid*, CHPh:CH·C(COOH):CH·C$_6$H$_4$·NO$_2$, obtained from sodium phenylisocrotonate, acetic anhydride, and meta-nitrobenzaldehyde, crystallises from benzene in greenish-yellow plates and melts at 156·5°.

a-Phenyldihydro-β-naphthoic acid, $C_6H_4\begin{subarray}{l}\text{CH}=\!=\text{C·COOH}\\ \text{CHPh·CH}_2\end{subarray}$, or $C_6H_4\begin{subarray}{l}\text{CHPh·CH·COOH}\\ \text{CH}=\!=\text{CH}\end{subarray}$, produced by molecular rearrangement of dibenzylidenepropionic acid under the influence of glacial acetic and concentrated sulphuric acids, separates from benzene in a crystalline powder melting at 191°; oxidation with alkaline potassium permanganate converts it into orthobenzoylbenzoic acid.

3 : 1-Phenylbenzylidenecrotonolactone, $CPh\begin{subarray}{l}\text{CH·C:CHPh}\\ \text{O}-\text{CO}\end{subarray}$, obtained by adding bromine (1 mol.) to a solution of dibenzylidenepropionic acid in chloroform and then evaporating the solvent, crystallises in golden-yellow leaflets and melts at 150°; concentrated sulphuric acid dissolves it unchanged, developing an intense, reddish-yellow coloration.

Phenacylcinnamic acid, COPh·CH$_2$·C(:CHPh)·COOH, prepared by hydrolysing the foregoing lactone, crystallises from alcohol in small prisms and melts at 171°; it forms colourless solutions with alkali carbonates, and becomes intensely yellow with caustic alkalis, yielding salts of the hydroxylic modification, OH·CPh:CH·C(:CHPh)·COOH. Re-

generation of the lactone is brought about by concentrated sulphuric acid and by hot acetic anhydride. The *barium* and *silver* salts are anhydrous; the *methylic* salt crystallises in small prisms melting at 79·5—80°, and yields the *semicarbazone* in colourless needles melting at 179°. *Phenylbenzylidenepyridazone*, $N{<}^{CPh\cdot CH_2}_{NH—CO}{>}C{:}CHPh$, produced on heating an alcoholic solution of methylic phenacylcinnamate with hydrazine hydrate, crystallises from absolute alcohol in white needles and melts at 177°; it is also formed when an alcoholic solution of the semicarbazone is boiled with a small quantity of ammonia. In addition to the phenacylcinnamic acid already described, an *isomeride* is produced when phenylbenzylidenecrotonolactone is hydrolysed, and crystallises from a mixture of benzene and petroleum in small, white needles melting at 127°; acetic anhydride containing a trace of concentrated sulphuric acid converts it into an *isomeride* of phenylbenzylidenecrotonolactone, crystallising from absolute alcohol in long, greenish-yellow needles which melt at 163°.

3 : 1-*Phenylbenzylidenebutyrolactone*, $CHPh{<}^{CH_2\cdot C:CHPh}_{O——CO}$, obtained by reducing a solution of sodium phenacylcinnamate with the copper–zinc couple, crystallises from ether in small needles and melts at 126°; it is insoluble in water, and dissolves with difficulty in organic media.

Benzylidenephenacylcinnamic acid,

$$COPh\cdot C({:}CHPh)\cdot C({:}CHPh)\cdot COOH,$$
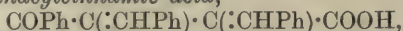
produced from phenacylcinnamic acid and benzaldehyde under the influence of caustic potash dissolved in methylic alcohol, separates from benzene in a crystalline powder and melts at 171°; concentrated sulphuric acid develops a dark red coloration which quickly becomes bright orange. The *silver* salt is unstable in the dry state.

Phenacylmethylcinnamic acid, $COPh\cdot CHMe\cdot C({:}CHPh)\cdot COOH$, prepared by the action of sodium ethoxide on methylic phenacylcinnamate and methylic iodide, followed by hydrolysis of the product, crystallises from benzene in microscopic needles, and melts, evolving gas, at 183—185°; the *sodium* salt contains $2\frac{1}{2}H_2O$, and the *methylic* salt melts at 90—91°.

Phenylbenzylidenemethylcrotonolactone, $CPh{<}^{CMe\cdot C:CHPh}_{O——CO}$, produced by the action of concentrated sulphuric acid on phenacylmethylcinnamic acid dissolved in acetic anhydride, crystallises from alcohol in long, yellow, highly refractive needles and melts at 128—128·5°; boiling sodium carbonate regenerates phenylmethylcinnamic acid.

M. O. F.

Phenacylbromocinnamic Acid. By JOHANNES THIELE and ERNST MAYR (*Annalen*, 1899, **306**, 171—175).—*Phenylbromobenzylidenecrotonolactone*, $C_{17}H_{11}BrO_2$, prepared by adding bromine to phenylbenzylidenecrotonolactone dissolved in chloroform, crystallises from alcohol in yellow needles and melts at 128·5°.

Phenacylbromocinnamic acid, $COPh\cdot CH_2\cdot C({:}CPhBr)\cdot COOH$, produced when bromine acts on phenylbenzylidenecrotonolactone or on

phenacylcinnamic acid in glacial acetic acid, crystallises from benzene in nodules; it melts and evolves gas at 137°, becoming solid immediately afterwards, and subsequently fusing at about 200°. Phenacylcinnamic acid is regenerated on reduction with zinc dust and glacial acetic acid.

Diphenylfurfurancarboxylic acid, described by Paal and Kapf, occurs as a bye-product in preparing the foregoing bromo-derivatives; it is also obtained on keeping a solution of phenacylbromocinnamic acid in caustic alkali at ordinary temperatures during 24 hours. The *methylic* salt melts at 63°.   M. O. F.

Phenacylhydrocinnamic Acid and the Dibromide of Dibenzylidenepropionic Acid. By JOHANNES THIELE and ERNST MAYR (*Annalen*, 1899, **306**, 176—193).—The *dibromide* of *dibenzylidenepropionic acid*, $CHPh\cdot Br\cdot CH:C(CHPhBr)\cdot COOH$, occurs in the mother liquor when 3 : 1-phenylbenzylidenecrotonolactone is recrystallised from alcohol, and is separated from the lactone by its insolubility in water; benzene deposits it in the form of a snow-white, crystalline powder which melts at about 194°, when it becomes red and evolves gas. Reduction with zinc dust and glacial acetic acid converts it into dibenzylidenepropionic acid.

Phenylbromobenzyl-α-crotonolactone, $\begin{matrix} CHPh\cdot CH \\ | \qquad\qquad \\ O\text{——}CO \end{matrix}{>}C\cdot CHPhBr$, obtained by the action of aqueous sodium carbonate on the dibromide of dibenzylidenepropionic acid dissolved in alcohol, becomes deep yellow at about 120°, and melts, evolving gas, at 130°; hydrogen bromide is eliminated very readily, phenylbenzylidenecrotonolactone being formed.

Phenacylhydrocinnamic acid, $COPh\cdot CH_2\cdot CH(CH_2Ph)\cdot COOH$, produced from phenylbenzylidenecrotonolactone, by reduction with zinc dust and glacial acetic acid, is also formed on reducing phenacylcinnamic acid; it crystallises from methylic alcohol in white needles and melts at 169·5°. The *methylic* salt melts at 68·5°, and yields the *phenylhydrazone* in white needles which melt and decompose at 106°.

3 : 1-*Phenylbenzyl-β-crotonolactone*, $\begin{matrix} CHPh:CH \\ | \qquad\qquad \\ O\text{——}CO \end{matrix}{>}CH\cdot CH_2Ph$, the labile lactone of phenacylhydrocinnamic acid, prepared by cautiously reducing phenylbenzylidenecrotonolactone with alcoholic sulphuric acid and zinc dust, is also formed when a few drops of concentrated sulphuric acid are added to a solution of phenacylhydrocinnamic acid in acetic anhydride; it crystallises from methylic alcohol in white needles, and melts at 100—101°. The lactone reduces alkaline potassium permanganate and ammoniacal silver solutions, and bromine dissolved in carbon bisulphide gives rise to hydrogen bromide; glacial acetic acid which has been saturated with hydrogen bromide resolves it into phenacylhydrocinnamic acid.

3 : 1-*Phenylbenzyl-α-crotonolactone*, $\begin{matrix} CHPh\cdot CH \\ | \qquad\qquad \\ O\text{——}CO \end{matrix}{>}C\cdot CH_2Ph$, the stable lactone of phenacylhydrocinnamic acid, arises from the labile modifi-

cation under the influence of boiling acetic anhydride, and is also
obtained by reducing the lactone of phenacylbromohydrocinnamic acid
with zinc dust and glacial acetic acid; it crystallises from light
petroleum in colourless leaflets, and melts at 67°. The stable lactone
decolorises alkaline potassium permanganate, but does not unite
with bromine; it is stable towards boiling dilute hydrochloric acid,
which resolves the labile modification into phenacylhydrocinnamic
acid, but undergoes hydrolysis when treated with a solution of hydrogen
bromide in glacial acetic acid.

The *dibromide* of α-acetoxyphenylcrotonic acid,

$$CHPhBr \cdot CHBr \cdot CH(OAc) \cdot COOH,$$
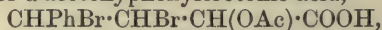
prepared by the action of hydrogen bromide in glacial acetic acid
on the dibromide of phenylhydroxycrotonic acid, forms a white,
crystalline powder; which becomes reddish at about 180°, and melts,
evolving gas, at 207°.   M. O. F.

Isomeric Diphenylcrotonolactones. By JOHANNES THIELE
(*Annalen*, 1899, **306**, 194—197).—Diphenylcrotonolactone, first ob-
tained by Klingemann, and subsequently by Erlenmeyer and Lux
(Abstr., 1898, i, 668), has been hitherto regarded as the βγ-unsaturated
lactone; as it has become possible to prepare a labile modification
(compare foregoing abstract), the author regards this substance as
having the constitution in question, the stable isomeride being unsatu-
rated in the αβ-position.

Labile *diphenylcrotonolactone*, $\begin{smallmatrix} CPh\colon CPh \\ | \qquad \\ CH_2-CO \end{smallmatrix}\!\!>\!\!O$, prepared by adding a
few drops of concentrated sulphuric acid to desylacetic acid suspended
in acetic anhydride, crystallises from a mixture of light petroleum and
benzene in small, white needles, and melts at 99·5—100·5°;
alcoholic potash regenerates desylacetic acid. The stable lactone,
$\begin{smallmatrix} CPh \cdot CHPh \\ || \qquad \\ CH-\!\!-CO \end{smallmatrix}\!\!>\!\!O$, obtained on treating the labile modification with
boiling acetic anhydride, is identical with the compound described by
Klingemann (Abstr., 1892, 1002).   M. O. F.

**Preparation of Phenylcinnamenylacrylic Acid and of
Diphenylbutadiene.** By JOHANNES THIELE and KARL SCHLEUSSNER
(*Annalen*, 1899, 306, 197—201).—The authors describe improvements
in Rebuffat's methods of preparing phenylcinnamenylacrylic acid,
diphenylbutadiene (diphenyldiethylene), and its dibromide (compare
Abstr., 1885, 1137, and 1891, 76).   M. O. F.

The Dibromide of Phenylcinnamenylacrylic Acid. By
JOHANNES THIELE and HEINRICH RÖSSNER (*Annalen*, 1899, **306**,
201—224).—2 : 5-*Diphenyl-2 : 5-dibromo-3-pentenoic acid*, the *dibromide*
of phenylcinnamenylacrylic acid, $CHPhBr \cdot CH\colon CH \cdot CPhBr \cdot COOH$,
prepared by the action of bromine (1 mol.) on phenylcinnamenylacrylic
acid dissolved in carbon bisulphide, crystallises from a mixture of
benzene and light petroleum, and melts at 174—175°, when it de-
composes; the *methylic* salt melts at 117—118°.

Diphenyldihydrofurfuran, $\begin{smallmatrix} CH \cdot CHPh \\ || \qquad \\ CH \cdot CHPh \end{smallmatrix}\!\!>\!\!O$, is formed from the dibromide

of phenylcinnamenylacrylic acid under the influence of sodium carbonate, sodium acetate, or caustic alkalis; it melts at 88—89°, and exhibits the behaviour of an unsaturated compound. *Tetrabromodiphenylfurfuran*, $\begin{matrix} CBr\dot{:}C(C_6H_4Br) \\ CBr\dot{:}C(C_6H_4Br) \end{matrix}\!\!>\!O$, obtained by exposing the finely powdered furfuran derivative to the action of bromine vapour during 24 hours, is identical with the compound, $C_{10}H_{10}Br_4O$, described by Perkin (Trans., 1890, 57, 954); oxidation with chromic acid dissolved in glacial acetic acid converts it into parabromobenzoic acid. *Pentabromodiphenylfurfuran*, $\begin{matrix} CBr\dot{:}C(C_6H_3Br_2) \\ CBr\dot{:}C(C_6H_4Br)- \end{matrix}\!\!>\!O$, produced when diphenylfurfuran is exposed to bromine vapour during 48 hours, crystallises from benzene in white needles and melts at 209—210°. *Tribromodiphenylfurfuran*, $\begin{matrix} CBr\dot{:}C(C_6H_4Br) \\ CH:C(C_6H_4Br) \end{matrix}\!\!>\!O$, prepared by reducing tetrabromodiphenylfurfuran with zinc dust and glacial acetic acid, crystallises from alcohol in slender, white needles and melts at 134°. The product of further reduction is *paradibromodiphenylfurfuran*, $\begin{matrix} CH\dot{:}C(C_6H_4Br) \\ CH:C(C_6H_4Br) \end{matrix}\!\!>\!O$, which crystallises from benzene in aggregates of long, slender needles, and melts at 201°; oxidation converts it into parabromobenzoic acid. The *dibromide* of diphenyldihydrofurfuran, $\begin{matrix} CHBr\cdot CHPh \\ CHBr\cdot CHPh \end{matrix}\!\!>\!O$, obtained on adding bromine (1 mol.) to a solution of diphenyldihydrofurfuran in carbon bisulphide, crystallises from alcohol in groups of small needles and melts at 110—111°.

Phenylbromocinnamenylacrylic acid, $CPhBr\cdot CH\cdot CH:CPh\cdot COOH$, a bye-product in the preparation of diphenyldihydrofurfuran from the dibromide of phenylcinnamenylacrylic acid, crystallises from methylic alcohol in nodules, and melts at 213—214°, evolving gas; the *potassium* and *sodium* salts contain $2\frac{1}{2}H_2O$, and the *methylic* salt melts at 127—128°.

Diphenylbutenincarboxylic acid, $CPh:C\cdot CH:CPh\cdot COOH$, prepared by heating phenylbromocinnamenylacrylic acid with alcoholic sodium methoxide during 20—30 hours at 170—180°, crystallises from benzene in slender, white needles; reduction with sodium amalgam in glacial acetic acid and alcohol converts it into 2 : 5-diphenyl-3-pentenoic acid (following abstract), which melts at 101—102°.

Cornicularolactone, $\begin{matrix} CPh:CH\cdot C:CHPh \\ CO\!-\!\!-\!\!-\!\!-\!O \end{matrix}$, produced by the action of diethylaniline on the dibromide of phenylcinnamenylacrylic acid at 150°, melts at 141—142°, and is identical with the compound described by Spiegel (Abstr., 1882, 1077). *Cornicularic acid*, $CH_2Ph\cdot CO\cdot CH:CHPh\cdot COOH$, prepared from the lactone by hydrolysis, crystallises from benzene in colourless plates, and melts at 122—123°; the *sodium* salt contains $2\frac{1}{2}H_2O$, and the *methylic* salt, which crystallises in white leaflets, melts at 95°.

Phenylbenzylpyridazone, $N\!\!<\!\!\begin{matrix} C(CH_2Ph)\cdot CH \\ NH\!-\!\!-\!\!-\!\!-\!CO \end{matrix}\!\!>\!CPh$, formed when

methylic cornicularate is heated with semicarbazide in glacial acetic acid, crystallises from alcohol in lustrous, white needles, and melts at 215°.

Methylic benzylidenecornicularate, $CHPh\!:\!CPh\cdot CO\cdot CH\!:\!CPh\cdot COOMe$, obtained from methylic cornicularate and benzaldehyde under the influence of pyridine, crystallises from alcohol in long, yellow needles, and melts at 138—139°.

Diphenyldianilidobutene, $C_4H_4Ph_2(NHPh)_2$, prepared by digesting diphenylbutadiene dibromide with aniline at 40—45°, crystallises from alcohol, and melts at 138—139°.   M. O. F.

Reduction of Dibenzylidenepropionic Acid and of Phenyl-cinnamenylacrylic Acid. By JOHANNES THIELE and JAKOB MEISEN-HEIMER (*Annalen*, 1899, **306**, 225—240).—*a-Phenylbenzylisocrotonic acid*, $CH_2Ph\cdot CH(COOH)\cdot CH\!:\!CHPh$, prepared by reducing an alcoholic solution of dibenzylidenepropionic acid with glacial acetic acid and sodium amalgam, crystallises from 85 per cent. alcohol in colourless prisms and melts at 124°.

2 : 1-*Bromophenyl-ac-tetrahydronaphthalene-3-carboxylic acid*,

$$C_6H_4\!\!<\!\!\begin{array}{l}CH_2\!\!-\!\!CH\cdot COOH\\CHPh\cdot CHBr\end{array},$$
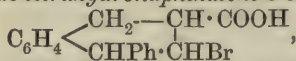
produced on adding bromine (1 mol.) to an ice-cold solution of phenyl-benzylisocrotonic acid in chloroform, crystallises from methylic alcohol in white needles and melts at 204—205°; the solution in sodium carbonate does not decolorise potassium permanganate.

1-*Phenyl-ac-tetrahydronaphthalene-3-carboxylic acid*,

$$C_6H_4\!\!<\!\!\begin{array}{l}CH_2\!\!-\!\!CH\cdot COOH\\CHPh\cdot CH_2\end{array},$$
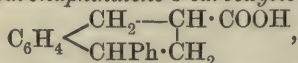
prepared by reducing the foregoing substance with glacial acetic acid and zinc dust, is also formed when benzylphenylisocrotonic acid is treated with a boiling mixture of glacial acetic and sulphuric acids during 7 hours; it crystallises from methylic alcohol in lustrous needles melting at 177°, and does not decolorise potassium perman-ganate. The *sodium* salt contains $6H_2O$, and the *methylic* salt melts at 82°; oxidation converts the acid into orthobenzoylbenzoic acid.

1 : 4-*Dihydro-1-phenylnaphthalene*, $C_6H_4\!\!<\!\!\begin{array}{l}CH_2\!\!-\!\!CH\\CHPh\cdot CH\end{array}$, obtained from

bromophenyltetrahydronaphthalenecarboxylic acid by the action of a boiling solution of sodium carbonate in slight excess, crystallises from methylic alcohol in lustrous needles and melts at 50°; its behaviour towards solutions of potassium permanganate and bromine is that of an unsaturated compound.

2 : 1-*Hydroxyphenyl-ac-tetrahydronaphthalene-3-carboxylic   acid*,
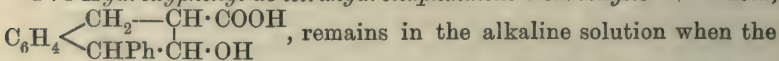
$C_6H_4\!\!<\!\!\begin{array}{l}CH_2\!\!-\!\!CH\cdot COOH\\CHPh\cdot CH\cdot OH\end{array}$, remains in the alkaline solution when the

foregoing hydrocarbon has been removed with ether; it crystallises from benzene in cubes and melts at 194°.

2 : 5-*Diphenyl-3-pentenoic acid*, $CH_2Ph\cdot CH\!:\!CH\cdot CHPh\cdot COOH$, pre-pared by reducing an alcoholic solution of *a*-phenylcinnamenylacrylic acid with glacial acetic acid and sodium amalgam, crystallises from alco-hol in plates and melts at 101·5°; it decolorises a solution of potassium

permanganate instantly. The *sodium* salt is readily soluble in water, and the *calcium* salt crystallises in slender, silky needles containing $2H_2O$, which is removed at 105°.

2 : 5-*Diphenyl-2-pentenoic acid*, $CH_2Ph \cdot CH_2 \cdot CH{:}CPh \cdot COOH$, obtained on heating the foregoing acid with 10 per cent. caustic soda during 20 hours on the water-bath, crystallises from light petroleum in lustrous, silky needles melting at 88°; it instantly decolorises an alkaline solution of potassium permanganate. The *sodium* salt contains $5H_2O$, and crystallises in lustrous needles; it is less readily soluble than the sodium salt of the isomeride.

2 : 5-*Diphenyl*-1 : 4-*pentanolide* (tetrahydrocornicularolactone),

$$CHPh \cdot CH_2 \cdot CH \cdot CH_2Ph$$
$$CO \text{————} O$$,
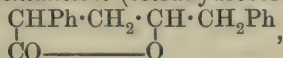
obtained from 2 : 5-diphenyl-3-pentenoic acid by the action of glacial acetic and concentrated sulphuric acids, is identical with the compound described by Spiegel (Abstr., 1882, 1077); the *silver* salt of the corresponding hydroxy-acid is amorphous. M. O. F.

Unsymmetrical Tetramethyldiamidodiphenylethane. By AUGUSTE TRILLAT (*Compt. rend.*, 1899, **128**, 1113—1115).—The *unsymmetrical tetramethyldiamidodiphenylethane*, $CHMe(C_6H_4 \cdot NMe_2)_2$, crystallises in colourless lamellæ melting at 68—69°; it is insoluble in water but readily dissolves in the ordinary organic solvents and also dilute acids, with which it forms well crystallised salts. It is prepared by mixing the volatile product of the oxidation of ethylic alcohol by chromic acid mixture with dimethylaniline and 20 per cent. sulphuric acid and warming the mixture for several days. The excess of aldehyde is distilled off, the mixture rendered alkaline and distilled with steam, and the residue crystallised from light petroleum and alcohol. The yield is 70 per cent. of the dimethylaniline employed. The *platinochloride* is slightly soluble in water and dilute hydrochloric acid, and crystallises in orange prisms decomposing at 210—211°. When the substance is oxidised with lead peroxide in acetic acid solution, a deep greenish-blue coloration is developed which disappears on warming the solution. G. T. M.

NOTE.—Two other isomerides of this base are already known, the symmetrical compound, $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot NMe_2$, melting at 50° (Abstr., 1879, 714, and 1887, 673), and the substance, melting at 87°, obtained by the action of zinc and hydrochloric acid on a mixture of dimethylaniline and carbon bisulphide (Tröger, Abstr., 1888, 286). G. T. M.

1 : 1-Diphenylbutene-1-one (3). By AUGUST KLAGES and E. FANTO (*Ber.*, 1899, **32**, 1433—1436).—*Ethylic α-acetyl-ββ-diphenyl acrylate*, $CMeO \cdot C(COOEt){:}CPh_2$, is best prepared by boiling benzophenone chloride in benzene solution for several hours with ethylic cupracetoacetate (obtained by mixing alcoholic ethylic acetoacetate with an ammoniacal aqueous solution of copper acetate at 0°), diluting with ether, filtering from cuprous chloride, shaking the solution repeatedly with water and then with dilute alkali, evaporating it, and cooling the residual oil with ice. It melts at 76°, forms an *oxime*

melting at 136—138°; with phenylhydrazine, it yields a yellow *pyrazolone* derivative, $\underset{NPh\cdot CO}{\overset{N=CMe}{\Big>}}C\!:\!CPh_2$, melting at 182—183°; it shows no disposition to form additive products with ethylic acetoacetate, benzylic cyanide, or deoxybenzoin, and yields the *acid* $CMeO\cdot C(COOH)\!:\!CPh_2$ when boiled with alcoholic potash. This acid melts at 143°, and its unstable *silver* salt at 169—170°; when the acid is distilled under diminished pressure, it yields 1:1-*diphenylbutene-1-one-3*, $CMeO\cdot CH\!:\!CPh_2$, which boils at 190° under 13 mm. pressure, melts at 33°, has a sp. gr. 1·080 at 16°/4°, and forms an *oxime* melting at 88°. C. F. B.

Hydrocinnamoin. By JOHANNES THIELE (*Ber.*, 1899, **32**, 1296—1297).—Cinnamaldehyde, when reduced with the zinc–copper couple in alcoholic solution, yields large quantities of *hydrocinnamoin*, $C_2H_2(OH)_2(CH\!:\!CHPh)_2$, a white, crystalline substance separating from alcohol in leaflets melting at 153—154°. The *diacetate*, which melts at 118—119°, forms small, white prisms, and the *dibenzoate* slender, colourless needles melting at 169—170°.

When the thick oil, which is the chief product in this reduction, is distilled, it yields a brown distillate, from which, after a time, white leaflets of a hydrocarbon of the formula $C_{18}H_{14}$ separate; this melts at 205—207°, and is sparingly soluble in alcohol; it is probable that it is phenyl-α-naphthylethylene. J. F. T.

Methylenequinones of the Dibenzyl and Stilbene Series, and the Corresponding Ketochlorides. By THEODOR ZINCKE (*J. pr. Chem.*, 1899, [ii], **59**, 228—244.—In analogy with previous work (this vol., i, 265), dihydroxytriphenylmethane, on bromination, yields tetrabromohydroxydiphenylmethylenequinone, 1 mol. of hydrogen bromide being eliminated,

$$CHPh(C_6H_4\cdot OH)_2 \longrightarrow OH\cdot C_6H_2Br_2\!:\!CPh\!:\!C_6H_2Br_2O.$$
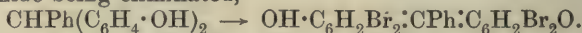
The reaction holds also for the stilbene and dibenzyl series.

Paradiamidotolane, when acted on by chlorine, yields the ketochloride, $C_6H_2Cl_2O\cdot CCl\!:\!CCl\cdot C_6H_2Cl_2O$, in two forms, melting at 246—247° and 212° respectively; each, on reduction, gives the same dihydric phenol, $C_{14}H_6Cl_6O_2$, melting at 248°. By the further action of chlorine, the phenol yields a white additive product melting at 222° and a red compound melting at 248°, the latter being converted into the former by the action of hydrogen chloride in acetic acid solution, whilst the white product, when heated with alcohol or aqueous acetone, loses hydrogen chloride and passes into the red compound, thus,

$$C_6H_2Cl_2O\!:\!CCl\cdot CCl\!:\!C_6H_2Cl_2O + 2HCl = C_6H_3Cl_2O\cdot CCl_2\cdot CCl_2\cdot C_6H_3Cl_2O.$$

The *diacetyl* derivative of the white compound forms thick, colourless crystals and melts at 176—177°. When heated with water, alcohol, or acetic acid, the red compound is converted into a colourless phenolic derivative, $OH\cdot C_6H_2Cl_2\cdot CO\cdot CO\cdot C_6H_2Cl_2\cdot OH$, which melts at 275°, and yields an azine when treated with orthophenylenediamine. When the phenol, $C_{14}H_6Cl_6O_2$, is treated with bleaching powder, it is converted into the compound $C_2Cl_2(C_6H_2Cl_3\!:\!O)_2$, which melts at 185°.

Paradihydroxystilbene, when treated with excess of chlorine, yields a hexachloro-derivative, $C_2H_2Cl_2(C_6H_2Cl_2\cdot OH)_2$, which, however, at

once passes into the more stable ketonic form, $C_2H_2Cl_2(C_6H_3Cl_2:O)_2$; this forms colourless needles, and decomposes when heated; when warmed with alcohol or acetone and water, it loses 2 mols. of hydrogen chloride and passes into the quinone, $C_2H_2(C_6H_2Cl_2:O)_2$, which resembles amorphous phosphorus in appearance. Treatment with stannous chloride reduces the quinone to tetrachlorodihydroxystilbene, whilst hydrogen chloride reconverts it into the hexachloride. When heated in sealed tubes with methylic or ethylic alcohol, the quinone is converted into colourless compounds of the formula $C_2H_2(OR)_2(C_6H_2Cl_2\cdot OH)_2$ where R = Me or Et. F. H. N.

Action of Isobutylic Bromide on β-Naphthylic Methylic Ether in Presence of Anhydrous Aluminium Chloride. By E. CAHEN (*Bull. Soc. Chim.*, 1898, [iii], 19, 1007—1008).—When isobutylic bromide is gradually added to a solution of β-naphthylic methylic ether and aluminium chloride in carbon bisulphide, the liquid heated at 65° for 3 hours, and the product fractionally distilled, a *substance*, $OMe\cdot C_{10}H_6\cdot CH_2\cdot CHMe_2$, is obtained which crystallises from alcohol in slender, prismatic needles melting at 66° and boiling at about 188° under 14 mm. pressure; it is decomposed with difficulty by boiling alkalis. N. L.

Condensation of Acenaphthenequinone and Hydrazine Hydrate. By JOACHIM HERMS (*Chem. Centr.*, 1899, i, 114—115; from *Diss. Kiel.*, 1898).—*Perinaphthoylhydrazimethylene*, $\begin{smallmatrix}C_{10}H_6\\CO-\end{smallmatrix}{>}C{<}\begin{smallmatrix}NH\\NH\end{smallmatrix}$

prepared by slowly adding hydrazine hydrate to acenaphthaquinone suspended in boiling alcohol, separates in small crystals, is easily soluble in hot alcohol, ether, benzene, or chloroform, slightly in hot water, and with concentrated sulphuric acid gives a characteristic violet coloration. Whilst by the action of benzaldehyde on this compound, only tarry products are obtained, with metanitrobenzaldehyde it forms *perinaphthoylmethylenemetanitroisobenzylideneazine*,

$$\begin{smallmatrix}C_{10}H_6\\CO-\end{smallmatrix}{>}C{<}\begin{smallmatrix}N\\N\end{smallmatrix}{>}CH\cdot C_6H_4\cdot NO_2,$$
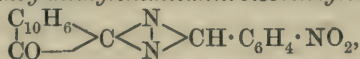
which crystallises in small, yellow needles, melts and decomposes at 253°, and is easily soluble in hot nitrobenzene, almost insoluble in alcohol or ether. Perinaphthoylhydrazimethylene is not oxidised as readily as Curtius's benzoylphenylhydrazimethylene, but when dissolved in benzene and treated with mercuric oxide, it yields *perinaphthoylazomethylene*, $C_{12}H_6O{<}\begin{smallmatrix}N\\N\end{smallmatrix}$, which separates from light petroleum in small crystals, melts at 79—80°, and is easily soluble in ether, alcohol, or chloroform, and insoluble in water; from the mother liquor, crystals melting at 94—102° were obtained. By the action of bromine on the azo-compound, *perinaphthoyldibromomethylene*, $C_{10}H_6{<}\begin{smallmatrix}CBr_2\\CO\end{smallmatrix}$, melting at 160—161°, is formed.

Perinaphthylenehydrazimethylenemetanitroisobenzylideneazine, possibly of the composition, $\begin{smallmatrix}NH\\NH\end{smallmatrix}{>}C{\underset{C_{10}H_6}{\frown}}C{<}\begin{smallmatrix}N\\N\end{smallmatrix}{>}CH\cdot C_6H_4\cdot NO_2$, obtained

by heating the nitroisobenzylideneazine with hydrazine hydrate for 6 hours at 110°, crystallises in yellow plates and melts at 215—216° with liberation of nitrogen. *Perinaphthylenebishydrazimethylene,*

$$C_{12}H_6\left(<^{NH}_{NH}\right)_2,$$
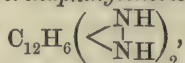
prepared by heating perinaphthoylhydrazine hydrate with alcohol on the water-bath, crystallises in pale yellow needles, melts at 192°, and is easily soluble in hot alcohol and hot chloroform, and insoluble in cold water. *Perinaphthylenebismetanitroisobenzylideneazine,*

$C_{12}H_6\left(<^{N}_{N}>CH\cdot C_6H_4\cdot NO_2\right)_2$, is obtained by heating a mixture of the dihydrazimethylene with metanitrobenzaldehyde on the water-bath; it crystallises in lustrous plates and prisms, melts at 246°, and is easily soluble in hot nitrobenzene and almost insoluble in alcohol or ether. Attempts to prepare perinaphthoylmonochloromethylene yielded a substance which melted at 109—110°. A comparison with the corresponding benzil and acenaphthenequinone derivatives shows that as the melting points rise in the one series they sink in the other, and *vice versâ.*　　　　　　　　　　　　　　　　E. W. W.

Structure of Terpenes and Allied Compounds. The Terpene from Solid Pinene Dibromide. By GODLEWSKI and GEORG WAGNER (*Chem. Centr.*, 1897, i, 1055; from *J. Russ. Chem. Soc.*, 1896, **29**, 121).—When Wallach's pinene dibromide (m. p. 169—170°) is treated with zinc dust and acid, the *terpene* $C_{10}H_{16}$ is produced; it melts at 65—66°, and boils at 153°. The hydrocarbon is indifferent towards potassium permanganate, but yields a solid additive compound with hydrogen chloride. If the new terpene does not contain an ethylenic linking, it represents a new type of hydrocarbon, to which the authors give the name *tricyclene*; such a substance would be the analogue of anthracene and phenanthrene.　　　　　　M. O. F.

Action of Hypochlorous Acid on Pinene. By ALEXANDER GINZBERG and E. WAGNER (*Chem. Centr.*, 1899, i, 50; from *J. Russ. Chem. Soc.*, 1898, **30**, 675—680).—By the action of hypochlorous acid on French turpentine of specific rotatory power $[\alpha]_D - 37°\ 50'$, and melting at 155·5—156·5°, a *chlorhydrin* is obtained which melts at 131—132° and has a specific rotatory power $[\alpha]_D + 88°\ 23'$. This compound, when mixed with an equal weight of the lævochlorhydrin of the same melting point prepared from dextropinene, forms the inactive chlorhydrin which is also obtained from dextropinene, and melts at 104—105°. By adding hypochlorous acid to an emulsion of pinene in water, treating the product with potassium carbonate, extracting with ether (compare preceding abstract), and distilling in steam, tricyclene dichloride, $C_{10}H_{16}Cl_2$, is obtained; it separates in monoclinic crystals (Wulff) and melts at 165—168°.
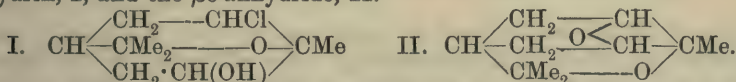
　　　　　　　　　　　　　　　　　　E. W. W.

Pinol Chlorhydrin. By ALEXANDER GINZBERG (*Chem. Centr.*, 1899, i, 50; from *J. Russ. Chem. Soc.*, 1898, **30**, 681—685).—By the action of hypochlorous acid on pinol, a *chlorhydrin* is obtained which crystallises from light petroleum in long needles, melts at 52—54°, is easily

soluble in alcohol, ether, chloroform, benzene, or ethylic acetate, and is more soluble in water than the pinene chlorhydrin ; the aqueous solution rapidly becomes acid. By the action of potassium hydroxide at the ordinary temperature, it forms the anhydride of pinolglycol obtained by Wallach from sobrerol dibromide, and pinene glycol is formed by treating the anhydride with dilute sulphuric acid (1:50), or by heating it with water on the water-bath for 7 hours, or from the chlorhydrin itself by boiling with water for 10 hours. Since the chlorhydrin, when oxidised with chromic acid at 0°, gives a product which, with phenylhydrazine acetate, forms a hydrazone, its composition is probably

$$\begin{array}{c} O\text{---}CH\text{------}CMeCl \\ | \qquad \qquad >CH_2 \qquad >CH{\cdot}OH. \\ CMe_2{\cdot}CH\text{------}CH_2 \end{array}$$ The oxidation product crystal-

lises in long needles and melts at 74—75·5°, and the hydrazone melts at 107—108°. E. W. W.

Structure of the Chlorhydrins and their Derivatives obtained by the Action of Hypochlorous Acid on Pinene. By ALEXANDER GINZBERG (*Chem. Centr.*, 1899, i, 50—51 ; from *J. Russ. Chem. Soc.*, 1898, **30**, 686—693).—The syrupy product obtained by the action of hypochlorous acid on pinene is a mixture of several compounds, only one of which, when treated with potassium hydroxide yields the *cis-* and *trans*-stereoisomerides of the crystalline chlorhydrin, I, and the $\beta\delta$-anhydride, II.

$$\text{I.} \quad CH\begin{array}{c} CH_2\text{---}CHCl \\ CMe_2\text{------}O \\ CH_2{\cdot}CH(OH) \end{array}CMe \qquad \text{II.} \quad CH\begin{array}{c} CH_2\text{------}CH \\ CH_2 \quad O \quad CH \\ CMe_2\text{------}O \end{array}CMe.$$

This anhydride cannot be obtained from the chlorhydrin, and is not identical with the anhydride of pinolglycol prepared from sobrerol dibromide. The structural formulæ of the dichlorhydrins are easily derived from these. E. W. W.

Caryophyllene Derivatives. By EDWARD KREMERS, OSWALD SCHREINER, and CHARLOTTE F. JAMES (*Pharm. Archives*, 1898, **1**, 209—215 ; compare Chapman, *Trans.*, 1895, **54**, 780). A comparison of the properties of the derivatives of caryophyllene and humulene shows that these substances are not identical. From caryophyllene of sp. gr. 0·9032 at 20°, specific rotatory power $[\alpha]_D - 8{\cdot}74°$, and specific refractive index n_D 1·50019, a nitrosochloride which melts at 158—160° was prepared by Wallach's method, using gaseous hydrogen chloride, however, instead of its solution. Caryophyllene *nitrosate* crystallises in slender needles, melts at 147—150°, is insoluble in alcohol and ether, rather soluble in benzene and chloroform, and slightly so in glacial acetic acid ; when boiled for a short time with alcoholic potash, it forms a compound which crystallises in white needles, melts at 220—223°, and is probably the oxime. The *nitrosite*, prepared by treating a mixture of equal volumes of caryophyllene and light petroleum with a concentrated aqueous solution of sodium nitrite and glacial acetic acid, crystallises in blue needles, forms a blue solution in alcohol, and melts at 107° ; the blue colour may be removed by recrystallising. Caryophyllene isonitrosite (Chapman, *Trans.*, 1895,

782), or bisnitrosite (Baeyer), obtained by heating the alcoholic solution of the nitrosite, crystallises in colourless forms and melts at 53—56°. *Caryophyllene nitrolbenzylamine* and *nitrolpiperidine* separate in white crystals and melt at 125—128° and 141—142° respectively. Humulene nitrosochloride melts at 164—165°, the nitrosate at 162—163°, the nitrosite at 120—121°, the isonitrosite at 165—168°, the nitrolbenzylamine at 136°, and the nitrolpiperidine at 153°.   E. W. W.

Essential Oils of Neroli and Petit Grain. By EUGÈNE CHARABOT and L. PILLET (*Bull. Soc. Chim.*, 1898, [iii], 19, 853—857).—In view of sundry discrepancies between the observations of previous experimenters, the authors have themselves distilled and examined nine specimens of oil of neroli and eight of oil of petit grain, a common adulterant of the former. The results obtained may be summarised as follows :

	Oil of neroli.	Oil of petit grain.
Sp. gr. at 15°	0·872—0·876	0·891—0·894
Rotation per 100 mm. at 15°	+1·42—4·06°	−4·45—6·00°
Index of refraction n_D at 18—21°	1·470—1·4745	—
Ethereal salts calculated as $C_{10}H_{17}$·OAc, per cent.	10·1—18·0	51·5—69·6
Parts of 80 per cent. alcohol required for solution at 20° ...	1·3—1·55	1—1·1

One of the specimens of oil of neroli was insoluble in alcohol ; the solubility appears to diminish with age. The difference in the rotatory powers of the two oils is shown by fractional distillation to be due to the fact that oil of neroli contains a larger proportion of dextrorotatory terpene and a smaller proportion of alcohols than does oil of petit grain. The alcohols, linalool and geraniol, contained in the two oils are qualitatively identical, although their relative proportions and the nature of the acids with which they are partially combined are different. It is to the ethereal salts present that the characteristic odours of the oils are due, since after hydrolysis both are found to possess a similar odour, recalling that of linalool.   N. L.

An Important Constituent of Oil of Neroli. By HEINRICH WALBAUM (*J. pr. Chem.*, 1899, [ii], 59, 350—352).—By shaking French oil of orange-blossoms with 30 per cent. sulphuric acid, a basic substance was obtained which proved to be the methylic salt of anthranilic acid ; it was also isolated from oil prepared by Schimmel and Co. from orange-blossoms which had been preserved in salt.

The substance was obtained as a colourless oil which gradually solidified. The crystals have a blue fluorescence, a property which is also exhibited in a marked degree by the alcoholic solution. The odour of the undiluted substance is not pleasant, but that of dilute solutions recalls that of orange-blossoms. It is easily prepared synthetically by the action of methylic alcohol and hydrogen chloride or sulphuric acid on anthranilic acid, and the synthetical substance has the same properties as the naturally occurring compound. It boils at 132° under a pressure of 14 mm., has a sp. gr. 1·168 at 15°,

melts at 24—25°, and resolidifies at 24° (compare E. von Meyer and G. Schmidt, Abstr., 1888, 371). A. L.

Oil of Neroli. By Ernst Erdmann and Hugo Erdmann (*Ber.*, 1899, **32**, 1213—1219).—Oil of orange-blossoms (Essence de Néroli pétales, Néroli Bigarade, &c.) contains a small quantity of *methylic anthranilate*, which was isolated and compared with the pure compound. It forms large crystals, melts at 24·5°, boils at 127° under 11 mm. pressure, and has a sp. gr. 1·163 at 26°. The crystals have a blue fluorescence, and the fluorescence of oil of orange-blossoms is no doubt due to the presence of this compound. About 2 grams of the hydrochloride were obtained from 1 kilo. of the oil. The *hydrochloride* melts at 178°, the *benzoyl* derivative at 99—100°.

Ethylic anthranilate melts at 13°, and boils at 136—137° under 13·5 mm. pressure. The odour of this compound is much fainter and coarser than that of the methylic salt.

Some specimens of oil of orange-blossoms contain small amounts of pyrroline derivatives, and these are always present in the oil of petit grain of commerce. The compound present is probably a nitrogen alkyl derivative, but has not yet been isolated. A. H.

Oil of Neroli. By Heinrich Walbaum (*Ber.*, 1899, **32**, 1512. Compare E. and H. Erdmann, preceding abstract).—The author claims priority for the observation that oil of orange-blossom contains methylic anthranilate. M. O. F.

Essential Oil of Thyme. By Henri Labbé (*Bull. Soc. Chim.*, 1898, [iii], **19**, 1009—1011).—From oil of thyme, 30 per cent. of thymol was extracted by treatment with aqueous potash, and the insoluble portion of the oil, on fractional distillation, yielded (1) 17 per cent. of a hydrocarbon boiling at 156—158°, which differs from pinene in forming a nitrosochloride melting at 106·5° and not yielding a hydrochloride; (2) 15 per cent. of menthene; (3) 21 per cent. of cymene; (4) 5 per cent. of linalool; (5) 8 per cent. of borneol, and (6) 4 per cent. of a residue boiling above 230°, and including, among other products, a small quantity of carvacrol. N. L.

Menthone from the Essence of Geranium from Bourbon. By Julian Flatau and Henri Labbé (*Bull. Soc. Chim.*, 1898, [iii], **19**, 788—790).—The essential oil of geranium from Bourbon, after hydrolysis, is treated with phthalic anhydride to remove geraniol and citronellol (compare Abstr., 1898, i, 618); the ketonic portion of the oil remains unaltered, and is extracted with ether and fractionated. The fraction boiling at 204—206° has an agreeable odour resembling that of menthone, the amount present in the original oil being about 6—7 per cent. The semicarbazone of this ketone is identical with that obtained from α-menthone; it melts at 180°, and crystallises from alcohol in white prisms. α-Menthone is most readily obtained from menthol by boiling this substance for 2 hours with potassium dichromate and 6 per cent. sulphuric acid; the oil is washed with water, extracted with ether, and fractionated. The semicarbazone is prepared by mixing together menthone, semicarbazide hydrochloride, and
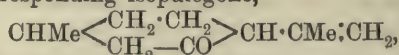
potassium acetate in dilute alcohol. Lævo-menthone, obtained by Beckmann's method from the corresponding menthol, yields a semi-carbazone melting at 184—184·5° which closely resembles its isomeride.

<div align="right">G. T. M.</div>

Occurrence of Isopulegol in Commercial Citronellal. By FERDINAND TIEMANN (*Ber.*, 1899, **32**, 825—826).—The author and R. Schmidt have already proved (Abstr., 1896, i, 383) that citronellal is readily converted into isopulegol. This substance has been studied by C. Harries, who has shown that it has the structure

$$CHMe \diagdown \genfrac{}{}{0pt}{}{CH_2——CH_2}{CH_2 \cdot CH(OH)} \diagup CH \cdot CMe \colon CH_2,$$
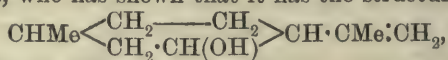
and that the corresponding isopulegone,

$$CHMe \diagdown \genfrac{}{}{0pt}{}{CH_2 \cdot CH_2}{CH_2——CO} \diagup CH \cdot CMe \colon CH_2,$$

exists in two stereoisomeric forms, of which one yields a semicarbazone which is sparingly soluble in ether and melts at 180°, and the other a semicarbazone which is more readily soluble in ether and melts at 171—172°, the mixture of the two semicarbazones melting at 173—174°.

When citronellal in commercial samples is separated from the accompanying terpenes by conversion into stable sodium citronellal-hydrosulphonate, a residue is obtained which has the odour, boiling point, and refractive index of isopulegol, but which probably contains, also, small quantities of geraniol and citronellol. The presence of isopulegol in the mixture was proved by oxidising it with chromic acid mixture, and converting the resulting isopulegone into the characteristic mixture of semicarbazones which melted at 173° and was separable into two portions having the properties described above.   A. L.

Separation of Citral and Citronellal. By JULIAN FLATAU and HENRI LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], **19**, 1012—1013).—The process recommended for the separation of the two aldehydes depends on the fact that when barium chloride is added to the aqueous solution of their mixed sodium hydrogen sulphite derivatives, the whole of the citral remains in solution, whilst the citronellal is quantitatively precipitated as the corresponding barium derivative, $C_{20}H_{38}O_8S_2Ba$. This is a white powder, insoluble in cold water and organic solvents, and only partially decomposed by boiling water, alkalis, and dilute acids; the citronellal may be recovered from it by treatment with 10 per cent. alcoholic potash.   N. L.

Separation of Citral from Citronellal and Methylheptenone. By FERDINAND TIEMANN (*Ber.*, **32**, 1889, 812—823).—Flatau and Labbé (preceding abstract and *Bull. Soc. Chim.*, 1899, [iii], **21**, 77) have proposed a method of separation in which a solution of the sodium hydrogen sulphite compounds of the two aldehydes is treated with barium chloride; the barium hydrogen sulphite derivative of citronellal is said to be precipitated, whilst the citral remains in solution. The author finds that the citronellal is not completely precipitated, and that the precipitate contains citral; moreover, neither aldehyde can be regenerated from the solution or precipitate without considerable loss.

It is found that citral is dissolved as the labile sodium citral-dihydrodisulphonate (compare this vol., i, 248) by a dilute solution of sodium sulphite containing sodium hydrogen carbonate, and can be regenerated from this solution with caustic soda ; citronellal is not affected by this solution. Further, a concentrated solution of sodium hydrogen sulphite containing sodium hydrogen carbonate dissolves citral, as the dilute solution does, but converts citronellal into the insoluble sodium hydrogen sulphite compound ; and, when shaken with a fairly strong solution of sodium sulphite while a current of carbonic anhydride is passed through, citral dissolves as before, and citronellal also dissolves, but as stable sodium citronellalhydro-sulphonate, which is not decomposed by caustic soda.

All these methods may be used for separating citral from citronellal. Perhaps the best method, available also in the presence of methyl-heptenone, terpene alcohols and terpenes, is first to shake the oil with a solution containing 100 grams of $Na_2SO_3 + 7H_2O$ and 35 grams of $NaHCO_3$ in 1 litre of water ; this dissolves the citral, which can be liberated from the solution by means of caustic soda. The oil is next shaken with a solution of 350 grams of $Na_2SO_3 + 7H_2O$ and 62·5 grams of $NaHCO_3$ in 1 litre of water ; a precipitate is formed of the sodium hydrogen sulphite compound of citronellal, from which the citronellal can be liberated by means of sodium carbonate. The residual oil, extracted with ether from the crystals and aqueous solution, is shaken with a solution of 1 part of commercial solid sodium hydrogen sulphite in $1\frac{1}{2}$ parts of water, the solution being cooled with ice ; in these circumstances, the sodium hydrogen sulphite compound of methylheptenone is precipitated ; this yields methylheptenone when treated with sodium carbonate.

It is found that oil of lemon-grass contains 0·2 and oil of lemons 0·4 per cent. of citronellal. C. F. B.

Natural Citral and the Composition of Oil of Lemon Grass. By FERDINAND TIEMANN (*Ber.*, 1899, **32**, 830—835).—The richest source of citral is oil of lemon grass, which contains 73—82 per cent. of citral, and little of other aldehydes. Citronellal and methyl-heptenone are also present and may be isolated as described in the preceding abstract. The residual oil contains 5—6 per cent. of terpenes (limonene, dipentene, sesquiterpenes, &c.), and also terpene alcohols (geraniol, and probably *l*-linalool and *l*-terpineol). By treatment with alcoholic potash, followed by distillation with steam and fractionation of the oil that distils over, methylheptenone and crude geraniol were obtained. Geraniol can also be obtained directly from oil of lemon-grass by treatment with benzoic anhydride and hydrolysis of the benzoates formed ; in this way, Schimmel and Co. have prepared it on the large scale during the last few years. C. F. B.

Stiehl's Three Lemon Grass Aldehydes. By FERDINAND TIEMANN (*Ber.*, 1899, **32**, 827—830).—It has already been shown that citriodoraldehyde and citral are identical (this vol., i, 247), and now Stiehl's experiments (this vol., i, 66) have been repeated step by step and determinations made of the physical constants of the aldehydic portions of the fractions termed citral and allolemonal, and also of

the so-called citriodoraldehyde; moreover, the melting points of the derived semicarbazones, citralidinecyanacetic acids, and β-naphthacinchonic acids as well as the physical constants of the pseudoionones and ionones obtained from each have also been observed. The results entirely confirm Semmler's and Doebner's conclusions (this vol., i, 223) and show that citriodoraldehyde, citral, and allolemonal are identical.

Stiehl has endeavoured to show that the sodium hydrogen sulphite compounds of the three fractions have different properties; this view does not bear investigation. The double compounds may be purified in a simple manner by means of a solution of common salt, which dissolves the admixed sodium sulphite and hydrogen sulphite, and the residue becomes microcrystalline, proving in each case to be the normal sodium hydrogen sulphite compound of citral. A. L.

Citronellylidenecyanacetic Acid. By FERDINAND TIEMANN (*Ber.*, 1899, **32**, 824—825).—Citronellylidenecyanacetic acid,

$$C_9H_{17}\cdot CH\text{:}C(CN)\cdot COOH,$$
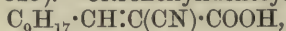
prepared by shaking citronellal with a solution of cyanacetic acid and sodium hydroxide in water, crystallises from benzene or alcohol in tabular crystals, melts at 137—138°, and is insoluble in water, but dissolves readily in alcohol and ether. Its acidic properties are less marked than those of citralidenecyanacetic acid. The *sodium* salt is sparingly soluble, and is especially characteristic; it separates in crystals on allowing the solution of the acid in moderately dilute warm soda to cool, whilst the salt of citralidenecyanacetic acid remains in solution under these conditions. The neutral solution of the ammonium salt gives nearly white precipitates with calcium chloride, copper acetate, and lead salts.

The detection of citral by means of citralidenecyanacetic acid is not rendered useless by the presence of citronellal in the oil, as the crude cyanacetic acid on recrystallisation from a mixture of benzene and alcohol gives without difficulty the pure citralidene derivative melting at 122°. A. L.

Transformations in the Carvone Series. By AUGUST KLAGES (*Ber.*, 1899, **32**, 1516—1521).—When carvone is heated with formic acid in a reflux apparatus, carvacrol is produced quantitatively; the same agent converts dihydrocarvone into carvenone. M. O. F.

Hydroxylaminocarvoxime, and its Conversion into Dihydrocarvyldiamine. By CARL D. HARRIES and F. MAYRHOFER (*Ber.*, 1899, **32**, 1345—1352. Compare Abstr., 1898, i, 568).—*Hydroxylaminocarvoxime,* $CH_2\text{:}CMe\cdot CH{<}^{CH_2-----C(NOH)}_{CH_2\cdot CH(NH\cdot OH)}{>}CHMe$, prepared by the action of hydroxylamine dissolved in methylic alcohol on carvone at ordinary temperatures, melts somewhat indefinitely at 60—65°, a specimen on one occasion melting at 83—84°; it boils at 190° under 6—7 mm. pressure, and a small quantity may be distilled under reduced pressure without decomposing, but large quantities decompose explosively. The *dibenzoyl* derivative crystallises from absolute alcohol, and melts at 171—172°; the *diphenylcarbimide* and *diphenylthiocarbimide* derivatives melt at 96—97° and 142—143° respectively.
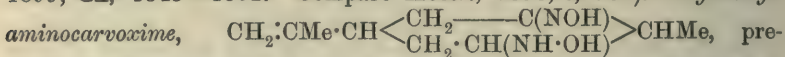
The *dioxime*, $CH_2{:}CMe{\cdot}CH{<}^{CH_2{\cdot}C(NOH)}_{CH_2{\cdot}C(NOH)}{>}CHMe$, obtained in
an impure form by Wallach and Schrader (Abstr., 1894, i, 536),
crystallises from absolute alcohol, melts and decomposes at 193—194°
when rapidly heated, and at 188° when the temperature is raised
more slowly ; it reduces Fehling's solution, and when treated with
boiling dilute sulphuric acid, yields the diketone melting at 194°.
The *dibenzoyl* derivative melts and decomposes at 118—120°. The
mother liquors of the dioxime yield an isomeric *compound*, $C_{10}H_{16}N_2O_2$,
which melts indefinitely at 153—155°.

Dihydrocarvyldiamine, $CH_2{:}CMe{\cdot}CH{<}^{CH_2{\cdot}CH(NH_2)}_{CH_2{\cdot}CH(NH_2)}{>}CHMe$, pre-
pared by reducing hydroxylaminocarvoxime with sodium and alcohol,
boils at 258—260° under atmospheric pressure, and at 122—123°
under 10 mm. ; it is a colourless, optically inactive liquid with a basic
odour, and readily absorbs carbonic anhydride from the atmosphere.
The *hydrochloride* is hygroscopic, and the *oxalate* forms a white
powder melting at 135—140° ; the *aurichloride* crystallises in long
needles, and the *picrate* begins to char at 229°, intumescing at 250°.
The *dibenzoyl* derivative melts at 275—276° ; the *diphenylcarbamide*
and *diphenylthiocarbamide* derivatives melt at 214—216° and 179—180°
respectively.

When dihydrocarvyldiamine hydrochloride is submitted to dry dis-
tillation, a *hydrocarbon* is produced isomeric with cymene ; it boils at
170—175°, and decolorises bromine and potassium permanganate.

M. O. F.

Racemisation of Camphor. By A. DEBIERNE (*Compt. rend.*,
1899, **128**, 1110—1113).—Anhydrous aluminium chloride is added to
a cooled solution of camphor in toluene, and the mixture heated at
80—85° for 15 hours ; the product, which has become optically
inactive, is then poured into water, the supernatant oil distilled
with steam, and the oily distillate rectified until all the toluene is
removed ; the residue, which solidifies on cooling, is crystallised from
alcohol. The final product has all the properties of camphor, but is
optically inactive ; on oxidation with nitric acid, it yields an inactive
camphoric acid which melts at 208°. This substance is shown to be
a racemic compound by resolving it into its active components by
means of cinchonine, and also by comparing it with the inactive acid
prepared by mixing equal parts of dextro- and lævo-rotatory camphoric
acids. It follows from this that the inactive camphor produced by
the action of aluminium chloride is a racemoid modification of dextro-
and lævo-camphor. G. T. M.

Physical Properties of some Camphors and Allied Substances.
By JULIUS W. BRÜHL (*Ber.*, 1899, **32**, 1222—1236).—The density,
molecular volume, refractive index for six wave-lengths, molecular
refraction and dispersion, and heat of combustion are given for a
number of oxygen compounds of the terpene series. In accordance
with its labile nature, carvone has a higher heat of combustion, a
greater molecular volume, and a lower molecular refraction and dis-
persion than carvacrol. Similarly, tanacetone has a greater molecular

volume and a lower molecular refraction and dispersion than carvo-tanacetone. In the series carone–dihydroeucarvone–dihydrocarvone–carvenone, carone has the highest heat of combustion and carvenone the lowest, corresponding with the order of stability of the four compounds; similarly, carone has the lowest and carvenone the highest molecular refraction; carvenone has also the highest molecular dispersion, those of the other three compounds being smaller and nearly equal; on the other hand, carone, although the most labile member of the series, has the lowest molecular volume, those of the other three compounds being larger and nearly equal to one another. The constants of dihydrocarvone and dihydroeucarvone are very similar, in spite of the wide difference between the formulæ assigned to them.

An examination of the constants of trimethylenecarboxylic and tetramethylenecarboxylic acids shows that the increments of molecular volume, molecular refraction, and molecular dispersion are very similar to those in the case of homologues of the aliphatic series.

The degree of saturation of the various compounds can be calculated from the physical constants. Carvone and carvacrol give numbers corresponding closely with the formulæ $C_{10}H_{14}O''|^=_2$ and $C_{10}H_{14}O'|^=_3$ respectively. The numbers for tanacetone are somewhat higher than those corresponding with the formula $C_{10}H_{16}O''$, and it is possible that a part of the substance has the enolic form $C_{10}H_{16}O'|^=$. Carvo-tanacetone also gives numbers higher than those corresponding with $C_{10}H_{16}O''|^=$. Dihydrocarvone and dihydroeucarvone give numbers corresponding with the ketonic formula $C_{10}H_{16}O''|^=$, but the values for carone and carvenone agree closely with those for the enolic formulæ $C_{10}H_{16}O'|^=$ and $C_{10}H_{16}O'|^=_2$.   T. M. L.

Derivatives of Amidocamphor. By PAUL DUDEN and W. PRITZKOW (*Ber.*, 1899, **32**, 1538—1543).—Amidocamphor is conveniently prepared by reducing isonitrosocamphor with zinc dust and caustic soda; the *hydrogen oxalate* crystallises from alcohol in leaflets melting at 194°. The picrate forms long needles and decomposes at 191°, whilst the *hydriodide* separates from water in beautiful, flattened needles and melts at 252—253°, when it decomposes.

Methylamidocamphor, $C_8H_{14} \begin{cases} CH \cdot NHMe \\ CO \end{cases}$, is a pale yellow oil which boils at 241° under 746 mm. pressure, and solidifies in a freezing mixture; it is indifferent towards Fehling's solution, and does not undergo condensation with benzaldehyde or ethylic acetoacetate. The *hydrochloride* crystallises in prisms, and becomes brown when heated, melting and decomposing at 228°; the *hydriodide, hydrogen oxalate,* and *picrate* melt at 201—202°, 191°, and 187° respectively. The *nitrosamine* crystallises from alcohol in six-sided prisms and melts at 78°, whilst the *acetyl* derivative forms colourless leaflets melting at 105°; the *carbamide* derivative crystallises from alcohol in small, rectangular plates and melts at 185°. *Methylamidoborneol,* $C_8H_{14} \begin{cases} CH \cdot NHMe \\ CH \cdot OH \end{cases}$, obtained by reducing methylamidocamphor in alcohol with sodium, boils at 257—258° under 744 mm. pressure.

Dimethylamidocamphor, $C_8H_{14}<^{CH \cdot NMe_2}_{CO}$, crystallises from petroleum and melts at 37°, boiling at 242—243° under 745 mm. ; the *hydrochloride* melts at 220—222°, whilst the *hydriodide* and *picrate* melt at 243° and 213° respectively. The *methiodide* crystallises in four-sided plates melting at 206°, and the corresponding *platinochloride* forms small, orange-coloured crystals which melt and decompose at 228°.

Dimethylamidoborneol, $C_8H_{14}<^{CH \cdot NMe_2}_{CH \cdot OH}$, prepared by reducing dimethylamidocamphor in alcoholic solution with sodium, crystallises from light petroleum in small prisms and melts at about 80°; it boils at 259—261° under 755 mm. pressure.　　　　　　M. O. F.

Camphenilone. By WILHELM JAGELKI (*Ber.*, 1899, **32**, 1498—1511). —Oxidation of camphene with dilute nitric acid leads to camphoic acid (Marsh and Gardner, Trans., 1891, **59**, 648 ; 1896, **69**, 74), a compound which has been called *carboxylapocamphoric acid* by Bredt and Jagelki (*Chem. Zeit.*, 1896, **20**, 842). In addition to the substance mentioned, there are formed dehydrocamphenylic acid, $C_{10}H_{14}O_2$, and the ketone, camphenylone, described by Majewski and Wagner (this vol. i, 629) ; camphenilic nitrite is the remaining product which has been isolated.

Camphenilic nitrite, $\begin{matrix} CH_2—CH \\ | \quad\quad >CMe_2 >C{:}CH \cdot O \cdot NO, \\ CH_2—CMe \end{matrix}$ melts at 66°, and boils at 147° under 12 mm. pressure ; it crystallises from petroleum in pale yellow needles, and detonates when heated strongly. Warm, concentrated sulphuric acid develops a beautiful, cherry-red coloration. Reduction with tin and hydrochloric acid or with zinc dust and acetic acid converts it into camphenilanaldehyde, obtained by Bredt and Jagelki on oxidising camphene with chromyl chloride (*loc. cit.*). Oxidation with potassium permanganate, or treatment with alcoholic potash, gives rise to camphenylone, which the authors call *camphenilone*.

The production of camphenilic nitrite depends on the initial formation of camphene nitrosite, arising from addition of the elements of nitrous acid to camphene ; this is established by a study of the behaviour of the hydrocarbon towards nitrous acid, which gives rise to the two following substances along with camphenilic nitrite.

Camphene *nitronitrosite*, $C_8H_{14}<^{C(NO) \cdot NO_2}_{CH \cdot NO_2}$, is a colourless substance which becomes blue when heated, and decomposes at 149°, yielding water and oxides of nitrogen ; it is insoluble in common media, but forms a blue solution in nitrobenzene. Camphene *nitrosite*, $C_8H_{14}<^{CH \cdot NO}_{CH \cdot NO_2}$, is an oil which decomposes when heated under reduced pressure at 50°, yielding water, nitrous oxide, and camphenilic nitrite ; the *potassium* derivative separates from alcohol in red crystals which detonate when heated, and the *benzoyl* derivative is a greenish-yellow, viscous liquid which cannot be distilled.

Camphenilone yields the *semicarbazone* in white crystals which melt

and decompose at 220—222°. The *hydrochloride* of the **oxime** is a white powder, and the *hydrobromide* is yellow ; the *platinochloride* crystallises from alcohol in yellow needles and melts at 106°.

Camphenilol, $CMe{<}^{CH_2 \cdot CH_2}_{}{>}CH$ ... prepared by reducing the ketone

with sodium in alcohol, crystallises in lustrous leaflets and melts at 84° ; it boils at 88·5—89° under 11 mm. pressure.

Camphenilone pinacone, $C_{18}H_{30}O_2$, obtained on reducing an ethereal solution of the ketone, crystallises in plates and melts at 134°; it boils at 200—202° under 11 mm. pressure.

Camphenilylic chloride, $CMe{<}^{CH_2 \cdot CH_2}_{}{>}CH$ ... produced on treating

camphenilol with phosphorus pentachloride, is a white, volatile substance resembling camphene ; it melts at 50°, and boils at 73° under 11 mm. pressure.

Camphenilene, $CMe{<}^{CH_2 \cdot CH_2}_{}{>}C$ ... is formed by the elimination of

hydrogen chloride from camphenilylic chloride by the agency of aniline at 175° ; it is a colourless liquid which boils at 142°, and decolorises solutions of bromine and of potassium permanganate.

When campheniloneoxime is oxidised with potassium permanganate, a considerable proportion of the ketone is regenerated, but on heating the substance with dehydrating agents, it loses the elements of water, and gives rise to a nitrile.

Camphoceenic nitrile, $\genfrac{}{}{0pt}{}{CH{-}{-}CH_2}{CMe \cdot CMe_2}{>}CH \cdot CN$ ... prepared by the action

of acetic chloride on campheniloneoxime, is a colourless oil which boils at 95—100° under 15 mm. pressure ; it instantly decolorises bromine and potassium permanganate. *Isocampheniloneoxime*, $C_9H_{15}NO$, a bye-product in the conversion of the oxime into nitrile, crystallises from alcohol in plates and melts at 165°; the *platinochloride* is a yellow powder.

Camphoceenic acid, $\genfrac{}{}{0pt}{}{CH{-}{-}CH_2}{CMe \cdot CMe_2}{>}CH \cdot COOH$ ... produced on hydrolysing

the nitrile or the amide, melts at 54°, and boils at 145° under 14 mm. pressure ; it instantly decolorises bromine and potassium permanganate. The *calcium* salt forms slender needles, and the *sodium* salt contains $1\frac{1}{2}H_2O$; the *silver* salt is sensitive towards light, and the *copper* salt forms a green powder soluble in chloroform. The *amide* crystallises from alcohol in lustrous leaflets and melts at 155°, when it decomposes ; it boils at 145°.

Dihydroxycamphoceanic acid, $\genfrac{}{}{0pt}{}{OH \cdot CH{-}{-}CH_2}{OH \cdot CMe \cdot CMe_2}{>}CH \cdot COOH$ ... prepared

by oxidising a solution of sodium camphoceenate with 1 per cent. potassium permanganate, separates from alcohol in white, transparent crystals, and melts at 163°, losing water at 186°.

Camphoceonic acid, $\genfrac{}{}{0pt}{}{CO{-}{-}{-}CH_2}{CHMe \cdot CMe_2}{>}CH \cdot COOH$ ... passes over at 184°

under 15 mm. pressure when dihydroxycamphoceanic acid is distilled, and forms white, lustrous crystals melting at 173°; the oxime crystallises from alcohol in long needles and melts at 150—156°, when it decomposes.

Hydroxycamphoceanolactone, $CMe{<}\begin{smallmatrix} CH(OH)\cdot CH_2 \\ CMe_2 \\ O \quad\quad CO \end{smallmatrix}{>}CH$, remains

undissolved when the product of distilling dihydroxycamphoceanic acid is treated with sodium carbonate; it melts at 58°, and boils at 165° under 13·5 mm. pressure.

When camphoceenic acid is oxidised with potassium dichromate and sulphuric acid instead of with potassium permanganate, dimethyltricarballylic acid is produced; the formula

$$COOH\cdot CMe_2\cdot CH(COOH)\cdot CH_2\cdot COOH$$
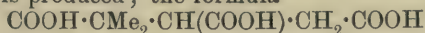
represents the constitution of this compound (compare von Baeyer, Abstr., 1897, i, 82). M. O. F.

Constitution of Camphorone. By CARL D. HARRIES and ISRAEL MATFUS (*Ber.*, 1899, **32**, 1343—1345. Compare Kerp, Abstr., 1896, i, 447).—*Camphoronehydroxylamine*, $\begin{smallmatrix} CH_2—CH_2 \\ CHMe\cdot CO \end{smallmatrix}{>}CH\cdot CMe_2\cdot NH\cdot OH$,

prepared by heating camphorone with ether, alcohol, and hydroxylamine in a reflux apparatus, melts at 119—120° and is identical with camphoroneoxime described by Koenigs and Eppens (Abstr., 1893, i, 361), and later by Kerp (*loc. cit.*); it reduces Fehling's solution when moderately heated, and develops a blue coloration with yellow mercuric oxide, indicating that the hydroxylamino-group has become attached to a tertiary carbon atom at the double linking, and occupies the β-position to the carbonyl radicle. The oxalate mentioned by Kerp melts at 154°.

7-Nitrosodihydrocamphorone, $\begin{smallmatrix} CH_2—CH_2 \\ CHMe\cdot CO \end{smallmatrix}{>}CH\cdot CMe_2\cdot NO$, obtained
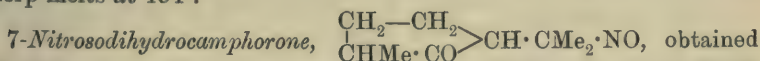
by oxidising camphoronehydroxylamine with sulphuric acid and potassium dichromate, sinters at 73° and melts at 80—82°, becoming blue; it dissolves readily in concentrated sulphuric and nitric acids, evolving gas.

In view of the results of these experiments, the authors express the constitution of camphorone and of the amine obtained on reducing its

hydroxylamino-derivative, by the formulæ $\begin{smallmatrix} CH_2—CH_2 \\ CHMe\cdot CO \end{smallmatrix}{>}C{:}CMe_2$ and
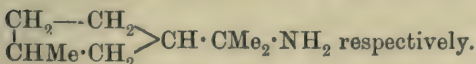
$\begin{smallmatrix} CH_2—CH_2 \\ CHMe\cdot CH_2 \end{smallmatrix}{>}CH\cdot CMe_2\cdot NH_2$ respectively. M. O. F.

Camphenylic Acid and its Derivatives. By J. MAJEWSKI and GEORG WAGNER (*Chem. Centr.*, 1897, i, 1056; from *J. Russ. Chem. Soc*, 1896, **29**, 124—132).—*Dehydrocamphenylic acid*, $C_{10}H_{14}O_2$, obtained from camphenylic acid by dehydration, crystallises in rhombohedric plates and melts at 147·5—148°; it is indifferent towards potassium permanganate, and is therefore regarded by the authors as a derivative of the class of substances called tricyclenes (this vol., i, 618).

Camphenylone, $C_9H_{14}O$ (compare Jagelki, this vol., i, 627), produced

on oxidising camphenylic acid with lead peroxide, melts at 36—38° and boils at 195° under 738 mm. pressure; it is indifferent towards an alkaline solution of potassium permanganate. Hot 40 per cent. nitric acid slowly oxidises the ketone, yielding oxalic acid along with an acid which melts at 114°. The *oxime* melts at 105—106°.

The *sodium* and *barium* salts of camphenylic acid crystallise in needles containing $1H_2O$, which is removed at 110°.

The constitution of the diketone from which camphenylic acid is obtained is expressed by the formula

$$CH_2 \left\langle \begin{array}{c} CH \text{———} CH_2 \\ \text{———} CMe_2 \\ CMe \text{———} CO \end{array} \right\rangle CO,$$

whilst camphenylic acid and camphenylone are represented by the formulæ

$$CH_2 \left\langle \begin{array}{c} CMe \text{———} \\ \text{———} CMe_2 \\ CMe \text{———} \end{array} \right\rangle C(OH) \cdot COOH \quad \text{and} \quad CH_2 \left\langle \begin{array}{c} CMe \text{———} \\ \text{———} CMe_2 \\ CMe \text{———} \end{array} \right\rangle CO$$

respectively. M. O. F.

Constitution of Isolauronolic Acid. By G. BLANC (*Bull. Soc. Chim.*, 1898, **19**, [iii], 699—706. Compare this vol., i, 536).— The author gives another demonstration of his constitutional formula for isolauronolic acid. This substance, when heated in sealed tubes at 300° for 4 hours, decomposes quantitatively into carbonic anhydride and an inactive hydrocarbon, C_8H_{14}, boiling at 108·5° under 758 mm. pressure. This compound is identical with the substance obtained by Damsky (Abstr., 1888, 293) and Koenigs and Meyer (Abstr., 1895, i, 155) from sulphocamphylic acid and by Moitessier from copper camphorate; it differs from the product derived from camphanic, lauronolic, and α-camphoramic acids, which is active and boils at 120°. The inactive hydrocarbon, when treated with a 1 per cent. solution of permanganate, yields dimethylhexanonoic acid, $COMe \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot COOH$, and this, on further oxidation with sodium hypobromite, gives rise to αα-dimethylglutaric acid. This result shows that the hydrocarbon possesses the constitution $CMe_2 \big\langle \begin{array}{c} CMe\vdots CH \\ | \\ CH_2 \text{–} CH_2 \end{array}$, and as it is derived from inactive lauronolic acid by loss of carbonic anhydride, it follows that the carboxyl group of this acid must be attached to carbon atom 3.
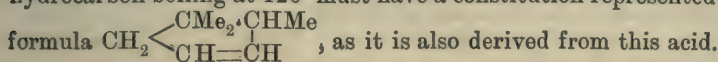
Moreover, the inactive hydrocarbon, when dissolved in carbon bisulphide and treated with acetic chloride in the presence of aluminium chloride, yields a ketone identical with that obtained from isolauronolic chloride with zinc methyl; the substance is further identified by means of its semicarbazone, which melts at 230—232° and not at 49° as previously stated (compare Abstr., 1897, i, 554). Since the entrant acetyl group certainly attaches itself to the carbon atom 3, the ketone must have the formula $CMe_2 \big\langle \begin{array}{c} CMe\vdots C \cdot COMe \\ | \\ CH_2 \text{–} CH_2 \end{array}$, and as the ketone is also obtained from isolauronolic chloride, it follows that isolauronolic acid must have the constitution $CMe_2 \big\langle \begin{array}{c} CMe\vdots C \cdot COOH \\ | \\ CH_2 \text{–} CH_2 \end{array}$. This view of the constitution of the inactive hydrocarbon explains its formation from sulphocamphylic acid,

$$CH{\Large<}{\begin{array}{l}CMe_2{\cdot}CMe{\cdot}SO_3H\\ \ \ \ \ \ \ \ |\\ CH_2{-}C{\cdot}COOH\end{array}}\quad,\ \text{and from camphoric acid,}$$

$$CH_2{\Large<}{\begin{array}{l}CMe_2{\cdot}CMe{\cdot}COOH\\ \ \ \ \ \ \ \ \ |\\ CH_2{-}CH{\cdot}COOH\end{array}}\ .$$
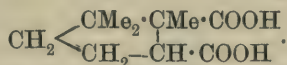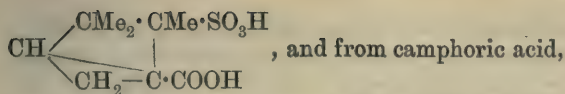
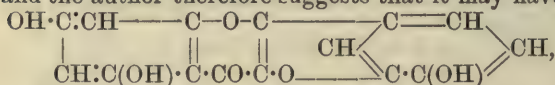If Bouveault's formula for camphoric acid is correct, the active hydrocarbon boiling at 120° must have a constitution represented by the formula $CH_2{\Large<}{\begin{array}{l}CMe_2{\cdot}CHMe\\ \ \ \ \ |\\ CH{=}CH\end{array}}$, as it is also derived from this acid.

G. T. M.

Oximes of Methylic Santonate and their Optical Behaviour. By EDGAR WEDEKIND (*Ber.*, 1899, **32**, 1411—1415).—When santonin-oxime, melting at 216—217°, is reduced with aluminium amalgam in alcoholic solution to which a little water has been added, a resinous product is obtained which melts at 180°. When the oxime is heated at 220° until the evolution of gas slackens, santonin is obtained, hydroxylamine having been eliminated through the agency of one of the molecules of water of crystallisation.

When methylic santonate in alcoholic solution is heated with hydroxylamine hydrochloride and chalk for several hours at 75°, the product poured into water and extracted with ether, and the ethereal extract concentrated and mixed with alcohol, two substances, $C_{16}H_{23}NO_4$, crystallise. The one which separates first, termed the α-oxime, is formed in much larger amount; it crystallises in tetrahedra, melts at 158—159°, has a specific rotation $[a]_D - 40{\cdot}66°$ in 1·5 per cent. alcoholic solution at 26°, and, when boiled with very dilute sulphuric acid, dissolves, yielding a solution which has a specific rotation $[a]_D + 42{\cdot}5°$ (in 1·6 per cent. solution) after boiling for 3 hours. The β-oxime melts at 193—194° and crystallises, with $1H_2O$, in needles; it has a specific rotation $+ 18{\cdot}15°$ in 0·826 per cent. alcoholic solution at 19°, and about $+ 72°$ after boiling with dilute sulphuric acid.

C. F. B.

Digitoflavone, a New Substance Isolated from Digitalis Purpurea. By FRANZ FLEISCHER (*Ber.*, 1899, **32**, 1184—1190). —*Digitoflavone*, $C_{15}H_{10}O_6 + H_2O$, isolated from the leaves of *Digitalis purpurea*, separates from 70 per cent. alcohol in yellow crystals, becomes anhydrous at 150°, and melts when rapidly heated to 320°, but if heated gradually chars at 300°; it dissolves in acetone and acetic acid, and less rapidly in ether, but is only very slightly soluble in boiling water. It is not a glucoside, does not interact with phenyl-hydrazine, and does not contain any methoxy-groups, but behaves as a trivalent phenol. The *tribenzoate* forms small, colourless needles, and melts at 219°, is insoluble in water, and only slightly soluble in alcohol; the molecular weight in naphthalene solution is normal. The *triacetate* crystallises in colourless needles, melts at 221—222°, and dissolves in alcohol, acetic acid, ether, or chloroform. The *tribenzenesulphonate* crystallises from a mixture of chloroform and ether in slender, colourless needles, and melts at 189°. The formula corresponds with that of a flavone derivative, and this conclusion is

supported by the formation of phloroglucinol and an acid, which is probably protocatechuic acid, on heating the substance with alkalis, There are therefore two hydroxyl groups in the 2 : 4-positions, but the orientation of the third and the nature of the remaining oxygen atom have not been definitely established. On heating the substance with concentrated hydrochloric acid at 350°, catechol appears to be formed, and the author therefore suggests that it may have one of the formulæ

$$OH \cdot C:CH\text{----}C\cdot O\cdot C\text{----}C\text{====}CH$$
$$CH:C(OH)\cdot C\cdot CO\cdot C\cdot O\text{----}C\cdot C(OH) \quad CH< \quad >CH,$$

or

$$OH\cdot C\text{====}CH\text{----}C\cdot O\cdot C\text{----}C\cdot CH\cdot CH$$
$$CH:C(OH)\cdot C\cdot CO\cdot C\cdot O\cdot C\text{----}C(OH) \quad >CH.$$

Like the members of the quercetin group, digitoflavone forms additive compounds with mineral acids, which are decomposed by water (Perkin, Trans., 1895, 645 ; 1896, 1439). T. M. L.

4 : 4-Dimethyl-3-keto-5-pyrrolidone and its Derivatives. By MAX CONRAD and KARL HOCK (*Ber.*, 1899, **32**, 1199—1208).— Alcoholic ammonia converts methylic bromodimethylacetoacetate into

4 : 4-*dimethyl-3-keto-5-pyrrolidone*, $NH<^{CH_2 \cdot CO}_{CO\text{---}CMe_2}$, which forms large, well-developed crystals melting at 144°. The *monoxime* melts at 230°, and the *phenylhydrazone* crystallises in long, white prisms melting at 168°. Dimethylketopyrrolidone is converted by boiling with hydrochloric acid into *amidomethyl isopropyl ketone* (amidodimethylacetone) *hydrochloride*, $CHMe_2 \cdot CO \cdot CH_2 \cdot NH_2,HCl$, which crystallises in nacreous, white scales melting at 165°. The base is a heavy oil which has strongly reducing properties, and has not yet been obtained in a pure state. The hydrochloride reacts with phenylhydrazine yielding isopropylphenylglyoxalosazone. Potassium cyanate converts the hydrochloride into *isopropylimidazolone*, $CHMe_2 \cdot C<^{CH \cdot NH}_{NH \cdot CO}$, which melts at 220°. When amidomethyl isopropyl ketone hydrochloride is boiled with aqueous soda and mercuric chloride, it yields 2 : 5-*di-isopropylpyrazine*, $^{CH\text{---}N \cdot CPr^\beta}_{CPr^\beta \cdot N \cdot CH}$, which is a colourless, highly refractive liquid with an odour like that of jasmine, boils at 206—207°, and has a sp. gr. 0·924 at 15°. On reduction, it is converted into *di-isopropylpiperazine*, $CHMe_2 \cdot CH<^{CH_2 \cdot NH}_{NH \cdot CH_2}>CH \cdot CHMe_2$, which is colourless and crystalline, melts at 58°, boils at 234°, and forms a strongly alkaline solution in water. The *urate* forms lozenge-shaped crystals, and the *hydrochloride*, $C_{10}H_{22}N_2,2HCl$, melts at 220°. *Nitrosoimidobisdimethylacetone*, $NO \cdot N(CH_2 \cdot CO \cdot CHMe_2)_2$, is obtained from the mother liquors from the preparation of dimethylketopyrrolidone, and crystallises in colourless needles melting at 112°.

Aniline readily reacts with methylic bromodimethylacetoacetate, forming *ethylic anilidodimethylacetoacetate*,

$$NHPh \cdot CH_2 \cdot CO \cdot CMe_2 \cdot COOMe,$$
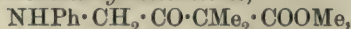
which melts at 64°. At 160 —180°, this compound loses the elements of

methylic alcohol, and is converted into 1-*phenyldimethylketopyrrolidone*, $NPh\begin{smallmatrix}CH_2 \cdot CO \\ | \quad | \\ CO-CMe_2\end{smallmatrix}$, which forms colourless crystals, melts at 104°, and boils at 315—316°. The *monoxime* crystallises in lustrous, white prisms melting at 168°, and the *phenylhydrazone* in colourless plates melting at about 196°. Methoxyaniline and ethoxyaniline react in a similar manner to aniline with methylic bromodimethylacetoacetate ; *orthomethoxyphenyldimethylketopyrrolidone*, $OMe \cdot C_6H_4 \cdot N\begin{smallmatrix}CH_2 \cdot CO \\ | \quad | \\ CO-CMe_2\end{smallmatrix}$, forms colourless crystals melting at 132°, whilst the corresponding *ethoxy*-compound melts at 130°. A. H.

Carboxylic Acids of Pyrrolidine. By RICHARD WILLSTÄTTER and WALTHER VON SICHERER (*Ber.*, 1899, **32**, 1290—1293).—β-Methyladipic acid, which is best obtained by the oxidation of pulegone with potassium permanganate, is readily brominated by Volhard's method, forming *ethylic* a_1a_2-*dibromo*-β-*methyladipate*, $C_2H_4(CHBr \cdot COOEt)_2$, a colourless, strongly refractive oil which boils at 202—204° or at 182—183° under pressures of 24 or 9 mm. respectively, and is converted on heating in a closed tube at 140° for 5 hours with methyl alcoholic ammonia into 3-*methylpyrrolidine*-2 : 5-*dicarboxylic acid*, a colourless substance separating from alcohol in needles, melting and decomposing at 239°, and closely resembling hygric and tropic acids in its properties ; the *platinochloride* separates from its aqueous solution in characteristic plates which decompose without melting when heated, and the *silver* salt is obtained from its aqueous solution on the addition of alcohol as a flocculent precipitate. J. F. T.

Action of Chloranil on Pyridine. By H. IMBERT (*Bull. Soc. Chim.*, 1898, [iii], **19**, 1008—1009).—When tetrachloroquinone (1 mol.) is added in small quantities at a time to an alcoholic solution of pyridine (2 mols.) and the liquid heated in a reflux apparatus for 8—10 hours, a small quantity of a *substance*, $C_6O_2(:C_5NH_3)_2 + 3H_2O$, is obtained which crystallises in slender, golden-yellow needles and is slightly soluble in cold, much more soluble in boiling, water and alcohol ; it is not decomposed at 105°, but yields pyridine when distilled. Its aqueous solution gives an intense red-brown coloration with ferric chloride solution. N. L.

Action of Phosphorus Pentachloride on 1-Alkylpyridones and 1'-Alkylquinolones. II. By OTTO FISCHER (*Ber.*, 1899, **32**, 1297—1307).—The method previously described (Abstr., 1898, i, 382) for the conversion of 1-alkylpyridones and 1'-alkylquinolones into halogen derivatives of pyridine and quinoline respectively by the action of the corresponding phosphorus haloid appears to be a general one.

[With W. HOERGER and R. JAEGER.]—2-*Chloropyridine* is best prepared by heating either 1-methyl-, 1-ethyl-, or 1-benzyl-pyridone mixed with phosphorus oxychloride with phosphorus pentachloride at 150—170° ; it has a sp. gr. 1·205 at 15°, and is readily reduced by sodium in alcoholic solution to piperidine. On heating for 20 hours with methylic iodide at 100°, it is converted into

2-iodopyridine methiodide, a colourless substance which separates from hot water in needles melting and decomposing at 207°; this readily reacts with bases, forming with aniline α-*anilidopyridine methiodide,* which crystallises from hot water in fine, white needles melting and decomposing at 176—179°; the *methochloride* formed from this by the action of silver chloride is obtained on evaporation of its aqueous solution as an oil which gradually solidifies and then melts at 65°. The *aurichloride* is a yellow, crystalline powder, and the *platinochloride* forms reddish-yellow needles melting at 214°. 2-Chloropyridine, when heated with zinc ammonium chloride for 5 hours at 220°, is quantitatively converted into 2-amidopyridine, which crystallises from light petroleum in leaflets melting at 56°, and when treated with potassium cyanate yields a sparingly soluble carbamide, $NH_2 \cdot CO \cdot NH \cdot C_5NH_4$, crystallising from moderately dilute alcohol in colourless prisms melting at 195°; with carbon bisulphide in alcoholic solution, 2-amidopyridine yields *dipyridylthiocarbamide,* $CS \cdot (NH \cdot C_5NH_4)_2$, a colourless substance crystallising from hot water or from dilute alcohol in prisms melting at 147°. 2-Amidopyridine gives with aldehydes characteristic condensation products, thus with salicylaldehyde, an *orthohydroxybenzylidene* compound is formed which crystallises from alcohol in light yellow needles melting at 69°, and with paranitrobenzaldehyde, a *paranitrobenzylidene* derivative which melts at 148°; these compounds are, however, very unstable.

2-Anilidopyridine, formed when 2-chloropyridine is heated with aniline zinc chloride in a sealed tube at 200°, is volatile in steam, and in that way is obtained in colourless leaflets melting at 108°; the *aurichloride* forms red prisms and melts at 149°, whilst the *platinochloride* is a red, crystalline powder melting at 202°; the *nitrosamine* crystallises in prisms melting at 102°.

1'-Benzylpyridone, which was mentioned as one of the substances from which 2-chloropyridine could be obtained, is best prepared by Decker's method from pyridine benzylochloride; it crystallises in colourless, glistening rhombohedra, and melts at 75—76°; the *mercurichloride* crystallises in white needles melting at 124°.

[With L. LEIDEL.]—2-*Bromopyridine,* which is prepared in the same way as the 2-chloro-derivative, is a highly refractive liquid having a sp. gr. 1·657 at 15°; the *hydrochloride* crystallises in needles; the *platinochloride* forms fine, red needles, the *aurichloride* separates in yellow leaflets melting at 173°, and the *mercurichloride* crystallises in needles.

Dibromopyridine, which is a bye-product in this reaction, crystallises in white needles, melts at 93°, and gives a *platinochloride* forming red needles, an *aurichloride* consisting of yellow crystals, and a *mercurichloride* forming colourless needles sparingly soluble in water or alcohol. In the same way, 2'-bromoquinoline is obtained from 1'-methylquinoline on treatment with phosphorus pentabromide.

[With PAUL KLITZSCH.]—2'-*Chloro-3-methylquinoline* is prepared in an analogous way to 2'-chloroquinoline (Abstr., 1898, 382) from 3-*methylquinoline.* This substance, which has not been previously described, is prepared by Decker's method from 3-methylquinoline methiodide by oxidation with potassium ferricyanide and sodium

hydroxide; it crystallises in colourless plates and melts at 90°, the *picrate* forms silky, yellow needles, and the *hydrochloride* short, colourless needles; 2'-chloro-3-methylquinoline crystallises from dilute alcohol in long, colourless needles which melt at 116°; the *hydrochloride* separates from alcoholic hydrogen chloride in long, colourless needles and is dissociated in water, and the *platinochloride* forms yellow leaflets. The chlorine atom in 2'-chloro-3-methylquinoline is readily replaceable, thus, with potassium hydrosulphide, 3-methylquinoline 2'-hydrosulphide is produced; it separates from hot alcohol or benzene in light yellow needles which melt at 210°; its *methiodide* crystallises from a mixture of alcohol and ether in yellow needles, and it further forms a *methosulphide*, crystallising in colourless needles which melt at 50°. On treatment with hydrogen peroxide, the hydrosulphide is quickly converted into the *bisulphide*, $C_{20}H_{16}N_2S_2$, which crystallises from hot alcohol in colourless leaflets and melts at 195°.

Methyl-α-naphthaquinoline and methyl-β-naphthaquinoline also react in the same way with phosphorus pentachloride, forming in the first instance α-*chlor-α-naphthaquinoline*, a substance crystallising in needles and melting at 105°, and in the second, the corresponding β-*derivative*, which crystallises from alcohol in colourless, glistening needles, and melts at 118°.   J. F. T.

Action of Phosphorus Pentachloride on 1-Alkylpyridones and 1'-Alkylquinolones. III. By OTTO FISCHER and KARL DEMELER (*Ber.*, 1899, **32**, 1307—1311).—Alkyl-4-pyridones and acridones differ from the 2-derivatives (see preceding abstract) in their behaviour with phosphorus pentachloride, since the displacement of the alkylchloride takes place only at high temperatures, thus with phosphorus pentachloride 4-methylpyridine gives 4-chloropyridine methochloride, which is analogous to the formation of chlorophenylphenazonium chloride from aposaffranone, a behaviour which seems to show that these compounds have, as Claus has suggested, a betaine-like constitution. 4-*Chloropyridine methochloride* decomposes above 200° with formation of hydrogen chloride, methylic chloride, and 4-chloropyridine; it is an extremely hygroscopic substance, the *aurichloride* crystallises in golden-yellow needles melting at 188—190°, and the *platinochloride* in reddish-yellow needles. The chlorine atom in γ-chloropyridine methochloride is very reactive, forming with aniline *anilidopyridine methochloride*, a substance which, although difficult to separate from aniline salts, forms a characteristic *aurichloride* crystallising in orange-coloured needles melting at 133°; the *platinochloride* forms bright yellow needles which melt at 197°.

N-Methylacridone reacts with phosphorus pentachloride in the presence of phosphorus oxychloride to form γ-*chloracridine methochloride*, a hygroscopic substance melting at 73°; its *aurichloride*, which melts at 227°, crystallises in orange-coloured needles, whilst the *platinochloride* forms a yellow, crystalline precipitate melting at 224—225°.

With aniline, γ-chloracridine methochloride gives γ-*anilidoacridine methochloride*, a crystalline substance which separates from dilute alcohol in yellow silky prisms melting at 235°; its *aurichloride* forms golden-yellow needles and melts at 182—183°, and its *platinochloride*, red-yellow needles and melts at 242°; the corresponding *base*, which

is free from oxygen, is precipitated as a yellow powder on the addition of ammonia to an alcoholic solution of the salt ; it crystallises from alcohol in yellow needles melting at 162—163°, and evidently possesses the constitutional formula $NMe{<}^{C_6H_4}_{C_6H_4}{>}NPh{-}{>}CH$.

γ-Naphthalidoacridine methochloride, from γ-chloracridine methochloride and β-naphthylamine, separates from dilute alcohol in red-yellow needles melting at 184—185°, and gives an *aurichloride* consisting of red-brown needles melting at 166—167° and a *platinochloride* forming brick-red octahedra which melt at 256°; the *base,* which crystallises from dilute alcohol in red needles and melts at 177°, must have a constitution analogous to that just indicated.   J. F. T.

Crystalline Form of Piperidine Hydrobromide and Methylallylaniline Picrate. By EDGAR WEDEKIND (*Ber.,* 1899, **32,** 1409—1411. Compare this vol., i, 449).—Piperidine hydrobromide crystallises in the rhombic system $[a:b:c = 0\cdot496:1:1\cdot5282]$, and shows no sign of hemihedry or hemimorphism. Methylallylaniline *picrate* (this vol., i, 353) forms hemihedral crystals of the monoclinic system $[a:b:c = 1\cdot3972:1:1\cdot7437]$.   C. F. B.

α- and β-Naphthaleneindigo. By HERMANN WICHELHAUS (*Ber.* 1899, **32,** 1236—1239. Compare Abstr., 1894, i, 42).—Better yields of the green indigo dyes previously described can be obtained by using Blank's method (Abstr., 1898, i, 589). Ethylic β-naphthylamidomalonate gives a yield of 83·5 per cent. of ethylic naphthylindoxylate melting at 157°, which when boiled with alkali, yields β-naphthaleneindigo, the yield being 54 per cent. of the theoretical. The dyeing properties of this compound with respect to colour and fastness are satisfactory. α-Naphthaleneindigo reacts with concentrated sulphuric acid at the ordinary temperature, yielding a *disulphonic acid,* which can be purified by solution in alcohol and precipitation with ether ; under similar conditions β-naphthaleneindigo yields a monosulphonic acid readily soluble in water or alcohol ; its solutions have a purple-red colour, but dye green; the alkali salts are obtained as flocculent precipitates when a solution of the acid is poured into solutions of sodium or potassium chloride. The *β-disulphonic acid* is formed when the indigo is left in contact with fuming sulphuric acid containing 25 per cent. of anhydride, and is best isolated in the form of its potassium salt, which crystallises in small needles ; with the same acid, but at a higher temperature, a *trisulphonic acid* is obtained. A *tetrasulphonic acid* may be prepared by the aid of sulphuric acid containing 40 per cent. of anhydride or of chlorosulphonic acid. All the sulphonic acids dye wool a bluish-green colour ; the tone is good, and the colours are very fast.   J. J. S.

Quinoline Perhaloids. By PERRY F. TROWBRIDGE (*J. Amer. Chem. Soc.,* 1899, **21,** 66—72).—*Quinoline hydriodide,* C_9NH_7,HI, obtained by heating quinoline with a slight excess of hydriodic acid, forms yellow, acicular crystals which dissolve in alcohol, and melts at 135°.

Quinoline methobromide, $C_9NH_7,MeBr$, prepared by passing methylic bromide into quinoline, crystallises in colourless needles melting at

$70°$; it is readily soluble in water, alcohol, ether, or chloroform, slightly so in acetone, and almost insoluble in light petroleum or benzene.

Quinoline hydrobromide tetrabromide, C_9NH_7,HBr,Br_4, obtained on adding a slight excess of hydrobromic acid to quinoline and saturating the mixture with bromine vapour, forms dark red, cubic crystals which melt at $39°$, and on exposure to the air give off bromine, the residue consisting of a mixture of lower perbromides melting at $88°$.

Quinoline hydrobromide dibromide, C_9NH_7,HBr,Br_2, obtained by saturating an aqueous solution of quinoline hydrochloride with bromine, forms fine, red crystals melting at $98—99°$.

Quinoline methobromide dibromide, C_9NH_7,CH_3Br,Br_2, obtained by saturating aqueous quinoline methobromide with bromine, separates in the form of a yellow precipitate, gradually changing to a heavy oil, which, on exposure to the air, is converted into a crystalline mass; it is almost insoluble in water or ether, but dissolves slightly in chloroform, and more so in alcohol, from which it crystallises in yellow needles melting at $108°$.

Quinoline hydriodide tetriodide, C_9NH_7,HI,I_4, gradually separates from a mixture of alcoholic iodine with either the aqueous hydriodide or hydrobromide of quinoline; it crystallises in lustrous, black plates melting at $76°$.

Quinoline methiodide tetriodide, C_9NH_7,CH_3I,I_4, obtained by adding an excess of alcoholic iodine to aqueous quinoline metho-chloride, -bromide, or -iodide, form greenish-black crystals melting at $70°$.

Quinoline hydrochloride bromide, C_9NH_7,HCl,Br, prepared by passing chlorine into a solution of quinoline and hydrobromic acid in much water, crystallises in fine, yellow needles melting at $101—102°$.

Quinoline methochloride bromide, C_9NH_7,CH_3Cl,Br, separates on saturating aqueous quinoline methobromide with chlorine; it crystallises in yellow scales melting at $112°$.

Quinoline hydrochloride iodochloride, C_9NH_7,HCl,ICl, formed when a warm aqueous solution of quinoline hydriodide is saturated with chlorine, crystallises in long, yellow prisms melting at $112°$.
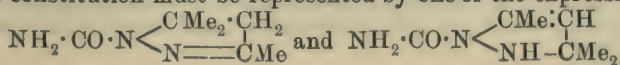
Quinoline methochloride iodochloride, C_9NH_7,CH_3Cl,ICl, prepared by saturating a warm, aqueous solution of quinoline methiodide with chlorine, forms fine, yellow crystals.

Quinoline hydrobromide iodobromide, C_9NH_7,HBr,IBr, obtained by saturating aqueous quinoline hydriodide with bromine, crystallises in red crystals melting at $109°$.

Quinoline methobromide iodobromide, C_9NH_7,CH_3Br,IBr, prepared by saturating aqueous quinoline methiodide with bromine, crystallises in yellow plates melting at $108°$. T. H. P.

Behaviour of Mesitylic Oxide towards Semicarbazide. By CARL D. HARRIES and FRIEDRICH KAISER (*Ber.*, 1899, **32**, 1338—1339).—Scholtz has observed that the semicarbazone of mesitylic oxide, which melts at $156°$, on distillation, yields an isomeride melting at $129°$ (Abstr., 1896, i, 343); as this modification is not resolved into its components under the influence of acids, it is suggested that its constitution must be represented by one of the expressions

$$NH_2 \cdot CO \cdot N \!\! \diagdown {\begin{smallmatrix} CMe_2 \cdot CH_2 \\ N = CMe \end{smallmatrix}} \quad \text{and} \quad NH_2 \cdot CO \cdot N \!\! \diagdown {\begin{smallmatrix} CMe:CH \\ NH - CMe_2 \end{smallmatrix}}$$

When mesitylic oxide is treated with an aqueous solution of semi-carbazide hydrochloride in molecular proportion, it is dissolved in the course of 12 hours; if exactly neutralised with potassium carbonate, the solution yields the base derived from mesitylsemicarbazone on distillation. Whilst the semicarbazone melts and decomposes at 162—164°, the isomeric base melts at 130—131°; the latter also differs from the semicarbazone in forming a picrate, which crystallises in long, yellow prisms, and melts at 136—137°.   M. O. F.

Constitution of Tartrazine. By RICHARD ANSCHÜTZ (*Annalen*, 1899, **306**, 1—5. Compare Abstr., 1897, i, 258; also Gnehm and Benda, Abstr., 1898, i, 209).—*Aminotartrazinogenic* (1-*parasulpho-phenyl*-4-*amidopyrazolone*-3-*carboxylic*) *acid*,

$$SO_3H \cdot C_6H_4 \cdot N {\overset{\displaystyle N=C \cdot COOH}{\underset{\displaystyle CO \cdot CH \cdot NH_2}{\Big<}}},$$
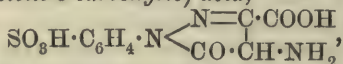
obtained in association with sulphanilic acid by reducing tartrazine with zinc dust, crystallises from dilute hydrochloric acid in small needles; the solutions in alkali carbonates become violet on exposure to air, and concentrated sulphuric acid develops a dark violet coloration with the acid. The *sodium* salt forms colourless crystals which become reddish.

It is probable that aminotartrazinogenic acid is the parasulphonic derivative of diphenylizindihydroxytartaric acid, obtained by Tafel (Abstr., 1887, 467).   M. O. F.

Pyrimidine. By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1899, **32**, 1525—1538).—2-*Orthomethoxyphenyl*-4-*methylpyrimidone*, OMe·C_6H_4·C$\overset{N \cdot CMe}{\underset{NH \cdot CO}{\Big<}}$CH, prepared by condensing anisamidine with ethylic acetoacetate under the influence of caustic soda, crystallises from dilute alcohol in aggregates of slender needles and melts at 202—203°; phosphorus oxychloride converts it into 2-*methoxyphenyl*-4-*methyl*-6-*chloropyrimidine*, OMe·C_6H_4·C$\overset{N \cdot CMe}{\underset{N=CCl}{\Big<}}$CH, which forms silky needles melting at 89—90°. 2-*Hydroxyphenyl*-4-*methylpyr-imidone*, OH·C_6H_4·C$\overset{N \cdot CMe}{\underset{NH \cdot CO}{\Big<}}$CH, obtained on reducing the chloro-base with hydriodic acid and phosphorus, forms small prisms and does not melt below 265°.

When acetylacetone is added to an ethereal solution of anisamidine, the *additive* compound, $C_8H_{10}N_2 + C_5H_8O_2$, separates in colourless leaflets (compare Pinner, Abstr., 1893, i, 735). 2-*Methoxyphenyl*-4 : 6-*dimethylpyrimidine*, OMe·C_6H_4·C$\overset{N \cdot CMe}{\underset{N:CMe}{\Big<}}$CH, prepared by heating the additive compound at 140°, melts at 96—97°; it dissolves in dilute hydrochloric acid, and the solution yields crystalline compounds with platinum tetrachloride and with potassium dichromate. 2-*Hydroxy-phenyl*-4 : 6-*dimethylpyrimidine*, OH·C_6H_4·C$\overset{N \cdot CMe}{\underset{N:CMe}{\Big<}}$CH, obtained on hydrolysing the methylic ether with concentrated hydrobromic acid, crystallises from dilute alcohol in silky needles and melts at 178—179°.

4 : 6-*Dimethylpyrimidine*-2-*carboxylic acid*, $COOH \cdot C \underset{N:CMe}{\overset{N \cdot CMe}{<}} > CH$,
prepared by oxidising hydroxyphenyldimethylpyrimidine with a 5 per
cent. solution of potassium permanganate, crystallises from warm
water in long, silky needles, which become opaque in air, owing to
loss of water; it melts at 145—146°. 4 : 6-*Dimethylpyrimidine*,
$CH \underset{N:CMe}{\overset{N \cdot CMe}{<}} > CH$, produced on submitting the carboxylic acid to
dry distillation, melts at 25° and boils at 159° under 768 mm.
pressure; it is miscible with water, forming a solution which is
neutral towards litmus. The *platinochloride* forms orange-yellow,
rhombic crystals, and melts at 103—104°; the *picrate* is sparingly
soluble, and crystallises in leaflets melting at 142—143°.

4-*Methyl*-2 : 6-*dichloropyrimidine*, $CCl \underset{N:CCl-}{\overset{N \cdot CMe}{<}} > CH$, obtained by
heating methyluracil with phosphorus oxychloride, crystallises from
petroleum in colourless needles and melts at 46—47°; the substance
boils at 219°, and the vapour in steam has an irritating odour.
Reduction with hydriodic acid and phosphorus converts it into hydroxy-
methylpyrimidine *hydriodide*, $OH \cdot C_4H_2MeN_2,HI$, which crystallises
in yellowish rhombohedra, sinters at 150°, and melts to a dark red
liquid at 185—187°. Fuming hydriodic acid alone reduces the dichloro-
base to methyliodopyrimidine, $C_4H_2IMeN_2$, the *hydriodide* of which
melts at 112—114° when rapidly heated; the *picrate* forms yellow
rhombs, and melts at 120—121°.

4-*Methylpyrimidine*, $CH \underset{N=CH}{\overset{N \cdot CMe}{<}} > CH$, prepared by reducing
methyldichloropyrimidine with zinc dust and water, boils at
141·5—142° under 762 mm. pressure, and has a sp. gr. 1·031 at 16°;
it is a mobile oil which mixes with water, and is indifferent towards
litmus. The *aurichloride* melts at 115°, and the *mercurichloride* crys-
tallises in slender needles melting at 198°; the *picrate* forms rhombic
leaflets, and melts at 131—134°. *Pyrimidine*-4-*carboxylic acid*,
$CH \underset{N}{\overset{N \cdot C(COOH)}{<}} \underset{CH}{\underset{}{}} > CH$, obtained on oxidising a boiling solution of
methylpyrimidine with 2 per cent. potassium permanganate, separates
from water in colourless crystals and melts at 240°; the *copper* salt
crystallises in pale blue rhombs which become opaque at 100°.

Pyrimidine, $CH \underset{N:CH}{\overset{N \cdot CH}{<}} > CH$, is formed from the carboxylic acid
on distillation, and melts at 20—22°, boiling at 123·5—124° under 762
mm. pressure; it has a penetrating, stupefying odour, and mixes with
water forming a solution neutral towards litmus. The *mercurichloride*
and *aurichloride* crystallise in needles, the latter salt melting at 226°; the
picrate forms yellow, silky needles, and melts at 156°. M. O. F.

Benzimidazoles. By REINHOLD WALTHER and TH. VON PULAWSKI
(*J. pr. Chem.*, 1899, [ii], **59**, 249—265).—Dibenzorthophenylene-
diamide is somewhat sparingly soluble in hot acetic acid and is
insoluble in acids, alkalis, benzene, ether, or water, and melts at 300°
(compare Abstr., 1891, 1130).

2'-Phenylbenzimidazole, $C_6H_4\underset{-N}{\overset{NH}{\diagdown}}\!\!>\!C\cdot Ph$, made by heating the preceding compound with hydrochloric acid in closed tubes at 200°, or by heating orthophenylenediamine with benzoic acid at 180°, crystallises in tablets, melts at 280° (compare Hübner, Abstr., 1881, 1131), is sparingly soluble in cold concentrated hydrochloric acid, but more readily in the hot liquid, yielding the hydrochloride.

Diphenacetorthophenylenediamide, $C_6H_4(NH\cdot CO\cdot CH_2Ph)_2$, crystallises in beautiful, white needles, and melts at 168°; it is somewhat readily soluble in hot benzene, alcohol, or acetic acid, and insoluble in alkalis, acids, water, or ether.

2'-Benzylbenzimidazole, $C_6H_4\underset{-N}{\overset{NH}{\diagdown}}\!\!>\!C\cdot CH_2Ph$, made by heating the preceding compound with hydrochloric acid at 140°, or, more simply, by heating orthophenylenediamine and phenylacetic acid at 180°, crystallises from benzene in well-formed, white needles, melts at 187°, and is very readily soluble in cold acetic acid, more sparingly in hot benzene, and insoluble in ether. The *hydrochloride*, $C_{14}H_{13}N_2Cl$, crystallises in beautiful tablets, the *nitrate*, $C_{14}H_{13}N_3O_3$, in beautiful, shining needles; both salts are hydrated and effloresce on exposure to air. The *sulphate*, *oxalate*, and *hydriodide* all crystallise well. The *platinochloride*, $(C_{14}H_{12}N_2)_2,H_2PtCl_6$, crystallises in small, yellow prisms. The *picrate*, $C_{14}H_{12}N_2,C_6H_3N_3O_7$, forms yellow leaflets and melts at 214°. When the base is heated in alcoholic solution with excess of iodine, it yields a *tri-iodide*, $C_6H_4\underset{-N}{\overset{NH_2I_3}{\diagdown}}\!\!>\!C\cdot CH_2Ph$, which crystallises from acetic acid in dark red prisms and decomposes, on prolonged heating with water, into the hydriodide of the base and free iodine.

Phenylenedibenzimidazole, $C_6H_4\!\left(C\underset{N}{\overset{NH}{\diagdown}}\!\!>\!C_6H_4\right)_2$, formed when orthophenylenediamine is heated with phthalic anhydride at 180°, is insoluble in the usual media, does not melt at 310°, and with mineral acids, yields well crystallised salts which dissociate in dilute solution partly into the monacid salt, and partly into free base. The *platino-chloride*, $C_{20}H_{14}N_4,H_2PtCl_6$, is a yellow, microcrystalline powder; the *picrate* crystallises in yellow needles and melts at 250°.

Ethylenedibenzimidazole, $C_2H_4\!\left(C\underset{N}{\overset{NH}{\diagdown}}\!\!>\!C_6H_4\right)_2$, formed by heating orthophenylenediamine with succinic anhydride at 180°, is insoluble in the ordinary media, and forms a white, amorphous substance melting above 310°. The *hydrochloride*, $C_{16}H_{14}N_4,2HCl$, forms beautiful, shining leaflets, the *platinochloride*, $C_{16}H_{16}N_4Cl_6Pt$, is a yellow, microcrystalline substance, and the *picrate*, $C_{28}H_{20}N_{10}O_{14}$, decomposes above 270°.

Dimetanitrobenzophenylenediamide, $C_6H_4(NH\cdot CO\cdot C_6H_4\cdot NO_2)_2$, crystallises in beautiful, white needles, melts at 240°, and is somewhat readily soluble in hot acetic acid or alcohol, sparingly soluble in hot benzene, and insoluble in water, acids, or alkalis.

2'-Metanitrophenylbenzimidazole, $C_6H_4\underset{-N}{\overset{NH}{\diagdown}}\!\!>\!C\cdot C_6H_4\cdot NO_2$, crystal-

lises from dilute alcohol in yellow needles melting at 204°, has feeble basic properties, and is scarcely soluble in mineral acids, dissolves readily in acetic acid or alcohol, and sparingly in benzene or water. The *picrate*, $C_{19}H_{12}O_9N_6$, forms yellow needles and melts at 254°.

Diorthonitrobenzophenylenediamide, $C_6H_4(NH \cdot CO \cdot C_6H_4 \cdot NO_2)_2$, crystallises in beautiful, pale yellow needles melting at 265°, and is soluble in warm acetic acid or alcohol, but insoluble in benzene, ether, acids, or alkalis.

2'-*Orthonitrophenylbenzimidazole*, $C_6H_4 <^{NH}_{-N}> C \cdot C_6H_4 \cdot NO_2$, crystallises from dilute alcohol in shining, brownish leaflets melting at 263°, and is very readily soluble in acetic acid or alcohol, sparingly so in hot benzene, and insoluble in water or ether. The *picrate* forms small needles and melts at 200°.

Monoparanitrobenzophenylenediamide, $NH_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_4 \cdot NO_2$, crystallises from boiling water in yellow needles, melts at 200°, and dissolves readily in cold acetic acid, alcohol, or hot benzene, but is only sparingly soluble in water. It yields the corresponding benzimidazole by continued boiling with strong hydrochloric acid.

Diparanitrobenzophenylenediamide, $C_6H_4(NH \cdot CO \cdot C_6H_4 \cdot NO_2)_2$, crystallises in beautiful, yellowish prisms, and is soluble in hot acetic acid or alcohol, but insoluble in water, acids, alkalis, benzene, or ether; when heated under pressure with strong hydrochloric acid, it yields the corresponding imidazole.

α-*Paranitrophenylbenzimidazole*, $C_6H_4 <^{NH}_{-N}> C \cdot C_6H_4 \cdot NO_2$, crystallises in yellowish-brown prisms, does not melt below 310°, and is readily soluble in cold acetic acid or alcohol, but insoluble in the other common media. It is identical with the substance obtained by Hinsberg and Funke by the action of paranitrobenzaldehyde on orthophenylenediamine. Its basic properties are very feeble, and it is scarcely soluble in strong hydrochloric acid. The *picrate*, $C_{19}H_{12}N_6O_9$, crystallises in yellow needles and decomposes at about 250°. **A. L.**

Benzimidazolecarboxylic Acid. By Otto Fischer (*Ber.*, 1899, 32, 1312—1315).—αβ-Naphthimidazole, $CH <^{NH}_{N}> C_{10}H_6$, is best prepared by heating together a mixture of αβ-naphthylenediamine, formic acid, and sodium formate at 130—140° for 10 hours; the *aurichloride* forms orange-red needles which melt at 269°, and the *platinochloride* separates from hot water in small, yellow needles. The *tetrahydro-compound*, $C_{11}H_{12}N_2$, obtained on reduction with sodium and amylic alcohol, forms slender, white needles melting at 196°; the *aurichloride* forms small, yellow needles, and the *platinochloride* orange-red needles.

Benzimidazole-1 : 2-*dicarboxylic acid*, $CH <^{NH}_{N}> C_6H_2(COOH)_2$, is obtained by the oxidation of naphthimidazole with chromic anhydride, and crystallises from hot water in white, glistening leaflets melting at 251°, it is readily soluble in alcohol, glacial acetic acid, or hot water, sparingly so in ether or light petroleum; the *silver* salt is a white, flocculent precipitate, and has the formula $C_9H_4N_2O_4Ag_2$, so

that the acid is dibasic, but as on titration only 1 mol. of normal potassium hydroxide is required, it is evident that one of the carboxyl groups is neutralised by the imido-group. On heating at 150°, the acid gradually passes into its *anhydride*, $C_9H_4N_2O_3$, which melts at 224—225° and sublimes in needles. On boiling the acid with aniline, a compound corresponding with phthalanil is formed, which crystallises from hot alcohol in needles. With phenols, the acid and its anhydride behave in the same way as phthalic acid and phthalic anhydride, forming products similar to phenolphthalein and fluorescein. The *dimethylic* salt crystallises from alcohol in white needles which soften at 231°; the fact that, on boiling this ethereal salt with dilute hydrochloric acid, the original acid is regenerated, shows that the substance is a true dimethylic salt and does not contain a methyl group attached to the imido-nitrogen. J. F. T.

Action of Orthophenylenediamine on Ethylic Bromodimethylacetoacetate. By MAX CONRAD and KARL HOCK (*Ber.*, 1899, **32**, 1208—1210).—2'-*Isopropylquinoxaline*, $C_6H_4\!\!<^{N\!:\!CH}_{N\!:\!C\cdot CHMe_2}$, formed by the action of orthophenylenediamine on ethylic bromodimethylacetoacetate in alcoholic solution, is a colourless oil, which boils at 269—270°, has a sharp taste, and smells of peppermint. On reduction, it yields *isopropyltetrahydroquinoxaline*,

$$C_6H_4\!\!<^{NH\cdot CH_2}_{NH\cdot CH\cdot CHMe_2,}$$
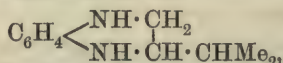
which melts at 75°, can be distilled without undergoing decomposition, and gives the characteristic blue coloration with ferric chloride.

A. H.

Quinazoline Derivatives. By ALEXANDER DRAWERT (*Ber.*, 1899, **32**, 1259—1266. Compare Gabriel and Stelzner, Abstr., 1896, i, 506).—Metaxylenephthaloic acid (Abstr., 1882, 848) is converted into the chloride by dissolution in warm benzene and treatment with phosphorus pentachloride; the solution is then well cooled, saturated with ammonia, mixed with slightly ammoniacal water, and the benzene removed by distillation with steam; the residue on cooling yields a brown deposit of *metaxylenephthalamide*, $C_6H_3Me_2\cdot CO\cdot C_6H_4\cdot CO\cdot NH_2$, which, on crystallisation from toluene, forms slightly brown plates melting at 152—153°.

2 : 4-*Dimethylorthamidobenzophenone*, $C_6H_3Me_2\cdot CO\cdot C_6H_4\cdot NH_2$, is prepared by mixing the moist and very finely divided amide with 10 per cent. sodium hydroxide and treating with sodium hypobromite, the mixture being well stirred and cooled; it crystallises in yellow plates, melts at 89°, and is readily soluble in the usual solvents; the *hydrochloride*, $C_{15}H_{15}NO,HCl$, forms colourless, compact crystals melting and decomposing at 170°; it gradually loses hydrogen chloride when kept; the *picrate* crystallises in small, yellow needles melting at 100—101°, and the *benzoyl* derivative in needles melting at 124°.

4-*Xylylquinazolone*, $C_6H_4\!\!<^{C(C_8H_9)}_{NH\cdot CO}\!\!>N$, obtained when the amidoketone is heated with carbamide, first at 175°, and finally at 195°, forms colourless needles melting at 260—261°; it has neither odour

nor taste, and is readily soluble in dilute acids or alkalis. The *hydro-chloride*, $C_{16}H_{14}N_2O,HCl$, forms small, reddish-yellow needles, and the *sulphate*, $(C_{16}H_{14}N_2O)_2,H_2SO_4$, orange-yellow needles melting and decomposing at 261°; the *dichromate* turns brown at 150° and blackens at 165°; the *picrate* crystallises in yellow needles, sinters at 210°, and melts at 214°.

2-Chloro-4-xylylquinazoline, $C_6H_4 {<} {\stackrel{\displaystyle C(C_8H_9)}{\displaystyle N{=}CCl}} {>} N$, is obtained when the quinazolone is boiled for half an hour with phosphorus pentachloride and oxychloride; it crystallises from ether in colourless needles melting at 126°, and is partially re-converted into the quinazolone by recrystallisation from boiling alcohol. The orthamidoketone is readily reduced by sodium amalgam (2·5 per cent.) and aqueous alcohol, yielding 2 : 4-*dimethylorthamidobenzhydrol*, $NH_2 \cdot C_6H_4 \cdot CH(OH) \cdot C_6H_3Me_2$, which crystallises in colourless prisms melting at 103°, is readily soluble in most organic solvents, but sparingly in concentrated hydrochloric acid; salts could not be obtained; its *acetyl* derivative forms colourless needles melting at 165°. The amidobenzhydrol condenses with carbamide, yielding 4-*xylyltetrahydro-2-ketoquinazoline*, $C_6H_4 {<} {\stackrel{\displaystyle CH(C_8H_9)}{\displaystyle NH{-}CO}} {>} NH$, which crystallises from alcohol in colourless prisms melting at 200°, and yields an unstable *hydrochloride* crystallising in needles; the *acetate*, $C_{16}H_{16}N_2O,C_2H_4O_2$, crystallises in colourless needles melting at 118—119°; the *picrate* crystallises in yellow needles melting at 160°. 4-*Xylyltetrahydro-2-thioquinazoline*, $C_6H_4 {<} {\stackrel{\displaystyle CH(C_8H_9)}{\displaystyle NH{-}CS}} {>} NH$, obtained by the action of thiocyanic acid on the amidobenzhydrol, crystallises in needles or rhombic plates, which sinter at 218° and melt at 222—223°; when an aqueous acetic acid solution is treated in the cold with bromine, 4-*xylyldihydro-2-bromo-quinazoline hydrobromide*, $C_6H_4 {<} {\stackrel{\displaystyle CH(C_8H_9)}{\displaystyle N{=}CBr}} {>} NH,HBr$, is obtained in the form of yellow, rhombic plates. The *base* separates from alcohol in crystals melting at 170—171°; the *hydrobromide* turns brown at 161°, melts and decomposes at 232—233°, is insoluble in acetic acid, and only sparingly soluble in absolute alcohol; when boiled with aqueous alcohol, saturated with soda, and again boiled, it yields the ketoquinazoline. **J. J. S.**

New Types of Anhydro-compounds. By STEFAN VON NIEMENTOWSKI [and in part with ST. KOZAKOWSKI] (*Ber.*, 1899, **32**, 1456—1493. Compare Abstr., 1895, i, 571, 1898, i, 210 and 337). —Acyl derivatives of β-orthamidobenzimidazoles are readily obtained when the compounds are heated with acids or acid anhydrides; they are characterised by the readiness with which they lose water and pass over into dianhydrides of the type $ {\stackrel{\displaystyle N{=}C \cdot C_6H_4}{\displaystyle C_6H_4 \cdot N{-}CR}} {>} N$. These anhydrides are usually obtained as bye-products during the preparation of the acyl derivatives, from which they may be separated by fractional crystallisation, and as a rule they are most readily obtained by

subjecting the crude acyl compounds to dry distillation. They stand in the same relationship to β-orthamidophenylbenzimidazole as does Hobrecker's ethylenetolylenediamine to metaparatolylenediamine. Most of the anhydro-derivatives are reconverted into the acyl derivatives by rupture of the ring when boiled with alkalis or mineral acids.

Orthonitrobenzorthonitranilide, $NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_4 \cdot NO_2$, obtained by the action of orthonitrobenzoic chloride on orthonitraniline, crystallises from acetic acid in pale yellow needles melting at 167—168°, is sparingly soluble in the usual solvents, most readily in acetone or acetic acid, dissolves readily in cold alkalis, and is only slowly hydrolysed when heated with concentrated hydrochloric acid at 120°. When exposed to sunlight, it changes colour and melts at a lower temperature; from this altered product, a small quantity of a substance melting at 133—136° has been isolated.

When the dinitranilide is reduced with zinc dust and 50 per cent. acetic acid, or with tin and hydrochloric acid in alcoholic solution, the only product is the corresponding diamido-derivative, but with tin and concentrated hydrochloric acid, stannous chloride and hydrochloric acid, or zinc dust and hydrochloric acid in alcoholic solution, the product is a mixture of the diamidoanilide and of β-orthamidophenylbenzimidazole; these may be extracted from the strongly alkaline liquid and separated by fractional crystallisation from alcohol. *Orthamidobenzorthamido-anilide* forms long, snow-white needles melting at 129—130°; it is readily soluble in most organic solvents, somewhat sparingly, however, in light petroleum or in ether, but readily in most acids. When submitted to dry distillation, it loses water and yields β-orthamidophenylbenzimidazole (*loc. cit.*). Its *hydrochloride*, $C_{13}H_{13}N_3O,2HCl + 2HO$, forms slender needles which, when kept in the mother liquor, become gradually transformed into thick, compact crystals. When heated, it loses water, and finally becomes transformed into the hydrochloride of orthamidophenylbenzimidazole. The *platinochloride*, $C_{13}H_{13}N_3O,H_2PtCl_6$, forms yellow prisms which do not melt at 330°.

The *silver* derivative of β-orthamidophenylbenzimidazole has been obtained as a white precipitate insoluble in alcohol. *Orthonitrobenzo-metanitroparatoluidide*, $NO_2 \cdot C_6H_3Me \cdot NH \cdot CO \cdot C_6H_4 \cdot NO_2$, crystallises in pale yellow prisms melting at 198°; it is very sparingly soluble in alcohol, more readily in acetone, toluene, or acetic acid, and very readily in alkalis, yielding yellow solutions. When reduced with tin and hydrochloric acid, it yields a mixture of β-orthamidophenylmeta-(para)tolimidazole (*loc. cit.*), orthamidobenzometamidoparatoluidide, and β-orthamidophenylmeta(para)oxytolimidazole, which may be separated by fractional crystallisation from alcohol. *Orthamidobenzo-metamidoparatoluidide* crystallises from alcohol in colourless rhomboidal plates melting at 137°; at higher temperatures, it loses water and is converted into the corresponding tolimidazole melting at 189°; it is readily soluble in chloroform or acetone, moderately in warm alcohol or benzene, and sparingly in ether, light petroleum, or water. When heated for several hours at 180° with concentrated hydrochloric acid, it is mainly converted into the tolimidazole, but part is decomposed into metaparatolylenediamine, aniline, and carbonic anhydride.

β-Orthamidophenylmeta(para)oxytolimidazole is formed in small quantities (about 10 per cent.) ; it crystallises in colourless, compact crystals melting at 240°, dissolves readily in chloroform, alcohol, or acetone, but is only sparingly soluble in water, ether, or benzene, and is insoluble in alkalis.

β-Orthacetamidophenylbenzimidazole, $C_6H_4 <^{-N}_{NH}> C\cdot C_6H_4\cdot NHAc,$ crystallises in needles melting and decomposing at 213—214°. *β-Orthacetamidoparatolylbenzimidazole,* $C_6H_4 <^{-N}_{NH}> C\cdot C_6H_3Me\cdot NHAc,$ may be readily separated from the anhydro-compound, which is formed at the same time, by its slight solubility in alcohol ; it crystallises in very slender needles melting at 252° and decomposing at 255°, is sparingly soluble in all organic solvents with the exception of hot acetic acid, dissolves readily in dilute acids and is not decomposed when boiled with alkalis.

Orthacetamidophenylmeta(para)tolimidazole, obtained by heating orthamidobenzometamidoparatoluidide with acetic anhydride and distilling the product, crystallises from toluene in yellow, fibro-crystalline masses softening at 187° and melting at 193°.

β-Orthopyruvamidophenylmeta(para)tolimidazole,

$$C_6H_3Me <^{-N}_{NH}> C\cdot C_6H_4\cdot NH\cdot CO\cdot COMe,$$
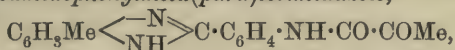
obtained by heating together pyruvic acid and amidophenyltolimidazole, crystallises in intensely yellow needles containing $2H_2O$, which it loses at 105° ; it melts and decomposes at 254°, is sparingly soluble in most organic solvents, but dissolves readily in ammonia and also in hot mineral acids. When heated with phenylhydrazine, it yields pyruvic acid phenylhydrazone and orthamidophenyltolimidazole (m. p. 189°).

β-Orthobenzamidophenylbenzimidazole, $C_6H_4 <^{-N}_{NH}> C\cdot C_6H_4\cdot NHBz,$ crystallises from alcohol in long, colourless needles melting at 251°. *β-Benzamidoparatolylbenzimidazole* crystallises from alcohol in needles melting at 268°, is very sparingly soluble in most organic solvents, insoluble in ammonia, and only sparingly soluble in concentrated hydrochloric acid. *β-Orthophenylacetamidophenylbenzimidazole,*
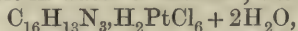
$$C_6H_4 <^{-N}_{NH}> C\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2Ph,$$
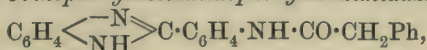
is obtained when the corresponding anhydro-compound is treated with benzoic chloride and alkali ; it crystallises from alcohol in slender needles melting at 240° and is readily soluble in most organic solvents.

Methenyl-β-orthamidophenylbenzimidazole, $\begin{matrix} N = C\cdot C_6H_4 \\ | \quad\quad | \\ C_6H_4\cdot N - CH \end{matrix} > N,$ crystallises in needles or plates melting at 227°, is very sparingly soluble in ether, readily in alcohol, benzene, or toluene, and very readily in chloroform or acetone ; it is insoluble in alkalis or ammonia, but dissolves in acids. When reduced with sodium and amylic alcohol, no definite product could be obtained, but on oxidation with chromic anhydride, carbonyl-β-orthamidophenylbenzimidazole is formed. When oxidised with alkaline permanganate, the same product is

obtained together with a scarlet substance melting at 300°. Benzoic chloride and alkali are without action on the methenyl compound; mineral acids hydrolyse it so readily that definite salts cannot be obtained. *Ethenyl-β-orthamidophenylbenzimidazole,* $\begin{array}{c} N = C \cdot C_6H_4 \\ C_6H_4 \cdot N \cdot CMe \end{array} \!\!> N,$ crystallises in prisms melting at 177—178°; its *hydrochloride* forms minute needles melting at 252°, and when treated with sodium nitrite yields the azimide of β-orthamidophenylbenzimidazole (*loc. cit.*). When the ethylene base is reduced with sodium and amylic alcohol, β-orthamidophenylbenzimidazole is formed. *Propenyl-β-orthamido-phenylbenzimidazole* forms hard, compact crystals melting at 147°, and is readily soluble in hot ether, benzene, alcohol, &c. Its *hydrochloride* crystallises with $\frac{1}{2}H_2O$, and yields two *platinochlorides*, namely, $(C_{16}H_{13}N_3)_2,H_2PtCl_6 + H_2O$ and $C_{16}H_{13}N_3,H_2PtCl_6 + 1\frac{1}{2}H_2O$. When oxidised with chromic anhydride, it gives a theoretical yield of carbonyl-β-orthamidophenylbenzimidazole. *Benzenyl-β-orthamidophenyl-benzimidazole* crystallises in long, silky needles melting at 239°, and is readily soluble in cold chloroform; the *hydrochloride,* $C_{20}H_{13}N_3,HCl,$ crystallises in small plates melting and decomposing at 235°. *Phenyl-ethenyl-β-orthamidophenylbenzimidazole,* $\begin{array}{c} N = C - C_6H_4 \\ C_6H_4 \cdot N \cdot C(CH_2Ph) \end{array} \!\!> N,$ obtained by heating a mixture of phenylacetic acid and β-orthamido-phenylbenzimidazole moistened with ethylic phenylacetate, crystallises in needles melting at 196°, and when oxidised with chromic anhydride, yields benzoic acid and carbonylamidophenylbenzimidazole. *Methenyl-β-orthamidoparatolylbenzimidazole* crystallises in feathery needles, softens at 200°, and melts at 215°; the *hydrochloride* and *sulphate* are readily soluble in water; the *platinochloride,* $C_{15}H_{11}N_3,H_2PtCl_6 + 3H_2O,$ darkens at 250°, but does not melt at 300°. During the preparation of the methenyl base, a bye-product, probably β-orthoformamidoparatolyl-benzimidazole, is obtained, which dissolves in acids, yielding a pale green, fluorescent solution. *Ethenyl-β-orthamidoparatolylbenzimidazole* crystallises in needles, prisms, or plates melting at 187—189°; its salts are readily soluble in water or alcohol; the *platinochloride,*
$$C_{16}H_{13}N_3,H_2PtCl_6 + 2H_2O,$$
forms pale yellow needles, and the *aurichloride* golden-yellow plates melting at 225°. The action of bromine on this base has been studied, but the products have not been examined in detail. *Benzenyl-β-orthamidoparatolylbenzimidazole* crystallises in snow-white, glistening needles melting at 240—241°; the *platinochloride,* $(C_{21}H_{15}N_3)_2,H_2PtCl_6,$ forms straw-coloured crystals melting and decomposing at 286°.

Methenyl-β-orthamidophenylmeta(para)tolimidazole crystallises in groups of concentric needles melting at 237° and is only sparingly soluble in ether; when heated with concentrated hydrochloric acid in sealed tubes, it is hydrolysed to *β-orthamidophenylmeta(para)tolimidazole hydrochloride* melting and decomposing at 245°. *Ethenyl-β-orthamido-phenylmeta(para)tolimidazole acetate* crystallises in needles which soften at 135° and melt at 142°; when heated at 105°, it loses acetic acid and yields the *base,* $C_{16}H_{13}N_3$, which crystallises, with $2H_2O$, in long needles melting at 160°. *Methenyl-β-orthamidoparatolylmeta(para)tolimidazole*

crystallises in needles melting at 212°, and on oxidation yields the corresponding carbonyl compound. *Ethenyl-β-orthamidoparatolyl-meta(para)tolimidazole* has not been obtained in a pure form; different fractions melting at 218°, 193°, and 172° gave practically the same results on analysis.

Carbonyl-β-orthamidophenylbenzimidazole, $\begin{smallmatrix} N \!=\!=\! C \cdot C_6H_4 \\ | \qquad\quad | \\ C_6H_4 \cdot N \!-\!\! CO \end{smallmatrix}\!\!>\!\! NH$, may

be obtained either by the oxidation of the corresponding methylene compound with chromic anhydride, or, still better, by the condensation of β-orthamidophenylbenzimidazole (1 part) with carbamide (2—3 parts); it crystallises from acetic acid with 1 mol. of acid, which it loses at 104° and then melts at 334°, is sparingly soluble in most solvents, and has feebly basic and also acid properties. It is more stable than the methylene derivative, and is only hydrolysed when heated at 190° with concentrated hydrochloric acid; two *hydrochlorides*, $C_{14}H_9N_3O,HCl$ and $C_{14}H_9N_3O,2HCl$, exist, but both are unstable, and give up all their acid at 105°. The *sulphate* forms colourless needles melting at 298°. When treated with nitric acid of sp. gr. 1·52, the carbonyl compound yields a *dinitro*-derivative, $C_{14}H_7N_5O_5$, which crystallises in minute needles melting at 315°; it is sparingly soluble in most solvents, and has a more pronounced acid character than the original substance. *Carbonyl-β-orthamidophenylmeta(para)tolimidazole*, $C_{15}H_{11}N_3O$, obtained by the action of carbonyl chloride on the amidophenyltolimidazole, crystallises in snow-white needles or glistening plates melting at 343°. *Carbonyl-β-orthamidoparatolylmeta(para)tolimidazole*, $C_{16}H_{13}N_3O$, forms small, crystalline aggregates melting at 182°; it differs from the other carbonyl derivatives in being readily soluble in most organic solvents.

Thiocarbonyl-β-orthamidophenylbenzimidazole, $C_{14}H_9N_3S$, obtained by heating amidophenylbenzimidazole with carbon bisulphide, first at 155° and then at 185°, crystallises in pale yellow needles melting at 291°; it is readily soluble in hot chloroform, acetone, or acetic acid, also in alkalis, but only sparingly in alcohol or benzene; it is very stable, and is not hydrolysed when heated at 170° with concentrated hydrochloric acid. When orthamidophenylbenzylimidazole is condensed with glycerol, nitrobenzene, and sulphuric acid by Skraup's method, *β-orthoquinolinebenzimidazole*, $C_6H_4\!\!<\!\!\begin{smallmatrix} -N \\ NH \end{smallmatrix}\!\!>\!\! C\cdot C_9NH_6$, is obtained, the yield being about 50 per cent. of the theoretical; it crystallises in concentrically arranged, brownish-yellow needles containing $1H_2O$, which it loses at 105°, melts at 124°, and is readily soluble in most organic solvents; the *sulphate*, $C_{16}H_{11}N_3,H_2SO_4$, crystallises in yellowish, nodular masses melting at 287°. J. J. S.

Some Amido-α-phenylbenzoxazole Derivatives. By OTTO KYM (*Ber.*, 1899, **32**, 1427—1432. Compare Pinnow and Wiskott, this vol., i, 500).—Dinitrophenylic benzoate is obtained in quantitative yield by heating 2:4-dinitrophenol with benzoic chloride for 2 hours at 180—200°. By reducing it cautiously with stannous chloride and hydrochloric acid, yellow *α-phenylmetamidobenzoxazole*,

$NH_2 \cdot C_6H_3 \underset{N}{\overset{O}{<}} > CPh$, melting at 151—152° is obtained. This reacts with acetic anhydride at the ordinary temperature, forming an *acetyl* derivative, which melts at 181—182°.

Trinitrophenylic benzoate, from picric acid and benzoic chloride, when cautiously reduced with stannous chloride, or tin and hydrochloric acid (Nietzki, Abstr., 1897, i, 277), yields a very little of the yellowish-green *a-phenylmetadiamidobenzoxazole*, $C_6H_2(NH_2)_2 \underset{N}{\overset{O}{<}} > CPh$, melting at 203—204°, the *diacetyl* derivative of which melts at 277—278°. This substance is better prepared by reducing, according to Nietzki's method, a-phenylmetadinitrobenzoxazole, which melts at 224—225° (not 218°), and is prepared by heating picramic acid with benzoic chloride and boiling the benzoylpicramic acid so obtained (which melts at 229—230°, not 220°) with acetic anhydride, or by boiling picramic acid with benzoic chloride in nitrobenzene solution.

Dinitrophenylic paranitrobenzoate, from 2 : 4-dinitrophenol and para-nitrobenzoic chloride, melts at 139—140°, and when reduced with stannous chloride and hydrochloric acid, yields *paramido-a-phenyl-metamidobenzoxazole*, $NH_2 \cdot C_6H_3 \underset{N}{\overset{O}{<}} > C_6H_4 \cdot NH_2$, which melts at 229—230°, and forms a *diacetyl* derivative melting at 278—279°.

<div align="right">C. F. B.</div>

Reaction of Alkaloids with Ortho-xylylenic Bromide. By MAX SCHOLTZ (*Arch. Pharm.*, 1899, **237**, 200—211).—The alkaloid was heated with ortho-xylylenic bromide in alcoholic, or occasionally chloroform, solution on the water-bath, and the whole then set aside. From the bromide so obtained, a chloride was prepared by treatment with silver chloride, or with silver oxide and water, and hydrochloric acid successively. The alkaloids react like the aliphatic amines (Abstr., 1898, i, 565). If they are tertiary bases, NR''', they yield di- or mon-ammonium bromides, $C_6H_4(CH_2 \cdot NR'''Br)_2$ or $CH_2Br \cdot C_6H_4 \cdot CH_2 \cdot NR'''Br$, according to the proportions which are taken. If they are di-acid bases, a number of products are possible, and several of them seem to be formed in the case of quinine, although none could be isolated; in the case of nicotine, the two compounds, $C_6H_4(CH_2 \cdot C_{10}H_{14}N_2Br)_2$ and $C_6H_4 \underset{CH_2}{\overset{CH_2}{<}} > C_{10}H_{14}N_2Br_2$, were actually obtained pure. In the case of the secondary base coniine, the compound $C_6H_4 \underset{CH_2}{\overset{CH_2}{<}} > NBr \underset{CH_2—CH_2}{\overset{CHPr \cdot CH_2}{<}} > CH_2$, is formed (1 mol. of caustic potash is added to neutralise the hydrogen bromide formed simultaneously). This compound, when heated with ammonia at 200°, yields a diamine, $C_6H_4 \underset{CH_2 \cdot NH \cdot CH_2—CH_2}{\overset{CH_2 \cdot NH \cdot CHPr \cdot CH_2}{<}} > CH_2$, which forms a nitroso-derivative, both NH-groups in which are converted into $N \cdot SO_2Ph$-groups when the diamine is suspended in dilute caustic potash and shaken with benzenesulphonic chloride.

The compounds obtained are enumerated below with their melting points under the names of the alkaloids from which they were prepared. From atropine : $C_6H_4(CH_2 \cdot C_{17}H_{23}NO_3Br)_2$, 145° ; *aurichloride*, 78° ;

platinochloride, 240—241°. From tropine: $C_6H_4(CH_2 \cdot C_8H_{15}NOBr)_2$, 230—231°; *platinochloride*, 246—247°; *aurichloride*, 228—229°; $CH_2Br \cdot C_6H_4 \cdot CH_2 \cdot C_8H_{15}NOCl$, 160°; *platinochloride*, 196°; *aurichloride*, 62°. From strychnine: $C_6H_4(CH_2 \cdot C_{21}H_{22}N_2O_2Br)_2$, 268—270°; $CH_2Br \cdot C_6H_4 \cdot CH_2 \cdot C_{21}H_{22}N_2O_2Br$, 200—203° From brucine: $C_6H_4(CH_2 \cdot C_{23}H_{26}N_2O_4Br)_2$, 228—229°; *platinochloride*. From narcotine: $C_6H_4(CH_2 \cdot C_{22}H_{23}NO_7Br)_2$, 160—162°. From papaverine: $C_6H_4(CH_2 \cdot C_{20}H_{21}NO_4Br)_2$, 207—208°, gives a yellow precipitate with caustic soda. From nicotine: $C_6H_4(CH_2 \cdot C_{10}H_{14}N_2Br)_2$, 95—97°; $C_6H_4 \cdot C_2H_4 \cdot C_{10}H_{14}N_2Br_2$, 158—159°; *platinochloride, aurichloride*. From coniine: *ammonium bromide* (see above); *platinochloride*, 193°; *diamine* boils at 215—218° under 25 mm. pressure; *dibenzenesulphonamide*, 117°. C. F. B.

Derivatives of Morphine. By EMMANUEL MERCK (*Arch. Pharm.*, 1899, **237**, 211—222).—The *hydrochlorides* of *propylic, isobutylic*, and *amylic morphine carbonates*, $OH \cdot C_{17}H_{17}NO \cdot O \cdot COOR, HCl$, were prepared by Otto and Holst's method (Abstr., 1892, 638). The *platinochloride* of the *propylic* salt crystallises with $2H_2O$. In a similar manner, the *acetyl* derivative of the *ethylic* salt can be obtained from a-acetylmorphine; it melts at about 150°; the *hydrochloride* melts and decomposes at 185°, the *platinochloride* at 210°; the latter crystallises with $1H_2O$.

The hydrochloride of benzoylmorphine (Sonntag, *Diss. Erlangen*, 1895), prepared by means of benzoic chloride, is actually precipitated from a solution containing excess of ammonia; it melts and decomposes at 176—177°; the base itself melts at 145°. Dibenzoylmorphine (Dankwortt, Abstr., 1891, 332), prepared by melting morphine with benzoic anhydride, forms a *hydrochloride*, $C_{31}H_{27}NO_5, HCl + H_2O$.

Dimorphine ethylenic ether, $C_2H_4(C_{17}H_{18}NO_3)_2$, is obtained by boiling morphine with alcoholic potash and ethylenic bromide; it melts at 188°. *Morphine benzylic ether*, $C_{17}H_{18}NO_2 \cdot O \cdot CH_2Ph$, is prepared by heating morphine with sodium ethoxide and benzylic chloride in alcoholic solution; both the base and its *hydrochloride*, "*peronine*," were prepared, but no analyses are given. Morphine ethylic ether, $OH \cdot C_{17}H_{17}NO \cdot OEt + H_2O$, melts at 93°, not 83°. Its *hydrochloride*, "*dionine*," melts and decomposes at 123—125°, and dissolves in 7 parts of water at the ordinary temperature. It will prove useful in therapeutics, as it is more soluble than any other derivative of morphine, except codeine phosphate, which has an acid reaction, and therefore causes pain when injected. C. F. B.

Non-Nitrogenous Decomposition Products of Morphine. V. By EDUARD VONGERICHTEN (*Ber.*, 1899, **32**, 1521—1524. Compare this vol., i, 307).—*Diacetylmorpholquinone*, $C_{18}H_{12}O_6$, obtained from diacetylmorphol by the method employed for preparing acetylmethylmorpholquinone from acetylmethylmorphol, crystallises in yellow needles and melts at 196°; a brownish-red coloration is developed on dissolving the substance in concentrated sulphuric acid. The *azine* produced when the quinone undergoes condensation with orthotolylenediamine, crystallises in yellowish needles and melts at 215—218°; the solution in concentrated sulphuric acid is deep blue, becoming red

when diluted with water.　When diacetylmorpholquinone is treated with sodium methoxide dissolved in methylic alcohol, a cherry-red solution is first formed, and quickly becomes deep blue; addition of dilute mineral acid precipitates dihydroxyphenanthraquinone, which differs from the methylic ether in that it dyes fibre with a mordant.

The author gives reasons for representing the constitution of morphol by the formula $\begin{array}{l} CH \cdot C_6H_4 \\ | \\ CH \cdot C_6H_2(OH)_2 \end{array}$ [CH:OH:OH = 2:3:4], and that of morphenol by the second expression in the last communication on the subject (loc. cit.).　　　　　　　　　　　　　　　　　　M. O. F.

Heroine [Diacetoxymorphine].　By G. WESENBERG (Chem. Centr., 1899, i, 123; from Pharm. Zeit., 1898, 43, 858).—Diacetoxy-morphine (heroine), $C_{17}H_{17}NO(OAc)_2$, is a white, crystalline, odourless powder, has an alkaline reaction, melts at 173°, is almost insoluble in water, slightly soluble in cold alcohol and ether, and easily in chloro-form, benzene, hot alcohol, and acids.　The normal salts are hygroscopic and difficult to crystallise, whilst the acid salts, like the acid oxalate, generally crystallise well.　The ordinary alkaloidal reagents form precipitates with solutions of the normal salts, a solution of iodine in potassium iodide giving a distinct turbidity with a solution containing only one part in 100,000.　The colour reactions of morphine are also shown by diacetoxymorphine, but the blue coloration with potassium ferricyanide and ferric chloride is only formed after some time and nitric acid gives a yellow coloration.　When treated with iodic acid, the diacetoxy-derivative, unlike morphine, does not liberate iodine, and when digested with pepsin-hydrochloric acid containing 0·2 per cent. of acid, about a fourth part is decomposed into morphine and acetic acid.　　　　　　　　　　　　　　　　　　　　　　E. W. W.

Alkaloids from Anhalonium Lewinii.　By E. KAUDER (Arch. Pharm., 1899, 237, 190—198. Compare Heffter, Abstr., 1895, i, 120; 1896, i, 267; 1898, i, 499).—Mezcal buttons, the dried heads of a Mexican cactus, Anhalonium Lewinii (or possibly A. Williamsi, as the two species can hardly be distinguished), were extracted with alcohol, the extract was freed from fat, and shaken with ammonia and chloroform, when a resin separated. The chloroform solution was shaken with water containing sulphuric acid, and the alkaloids so removed were separated into two groups, those of the first being readily soluble in ether, those of the second only slightly soluble in ether, but readily in chloroform.　The alkaloids of the first group were separated by crystallisation of their hydrochlorides from absolute alcohol; anhalonine separated first, then pellotine, and finally lophophorine.　The alkaloids of the second group were converted into sulphates and these crystallised from water; mezcaline sulphate crystallised first.　The succeeding crystallisations were shaken with ammonia and chloroform; a new alkaloid, anhalamine, remained undissolved.　The alkaloids which dissolved were converted into hydrochlorides and heated [with absolute alcohol; the hydrochloride of mezcaline went into solution, whilst that of anhalonidine remained undissolved.

Anhalamine melts at 186°, and is a strong base.　It dissolves to

some extent in boiling chloroform and benzene, and the solutions solidify to a gelatinous mass as they cool. C. F. B.

Derivatives of Ecgonine. By RICHARD WILLSTÄTTER (*Ber.*, 1899, **32**, 1635—1641).—The *aurichloride* of ethylic ecgonine methochloride is very slightly soluble in water, and crystallises in prisms melting at 176—177°. The *aurichloride* of ecgonine methochloride crystallises in thin flakes and melts with decomposition at 214—217°; it is somewhat soluble in hot water and on cooling separates with $1H_2O$.

Unlike ethylic ecgonine, its methiodide is not hydrolysed by boiling with water during 12 hours. Silver oxide, however, converts it into *ecgonine methylbetaine*, which crystallises in slender, colourless prisms, decomposes and melts at 278°, dissolves sparingly in water, very slightly in hot alcohol, and is insoluble in ether. By the action of concentrated hydriodic acid, the betaine is converted into *ecgonine methiodide*, a monobasic acid, which dissolves readily in water, crystallises in prisms, and decomposes at 238—239°.

Methylic dihydroxyanhydroecgonine methiodide melts and decomposes at 205—206°; it crystallises in four-sided prisms or six-sided tablets, and is very readily soluble in cold water; no trace of dimethylamine is eliminated, even after long boiling with strong potash. *Dihydroxyanhydroecgonine methiodide* decomposes at 255°, dissolves easily in water, but only slightly in boiling alcohol, and crystallises in square tablets; it is a monobasic acid, and does not form a lactone.

Dihydroxyanhydroecgonine methylbetaine resembles ecgonine methylbetaine; it is very easily soluble in water and slightly soluble in alcohol, from which it crystallises in tablets and tetragonal pyramids; it decomposes between 260° and 270°, is slightly hygroscopic, and has a neutral reaction.

In reply to Buchner (this vol., i, 423), it is suggested that the variation in melting point of the amide of Δ^1-cycloheptenecarboxylic acid, when prepared in different ways, is due to different degrees of purity and not to *cis-* and *trans-*, or to structural isomerism. Conductivity determinations gave for this acid $\mu_\infty = 375$, $100k = 0.000830$, whilst γ-cycloheptatrienecarboxylic acid (m. p. 55°, from ecgonine) gave $\mu_\infty = 377$, $100k = 0.00379$, and the δ-acid (m. p. 32°, from anhydroecgonine) gave $\mu_\infty - 377$, $100k = 0.00396$. T. M. L.

Emetine Octiodide; Extraction and Estimation of Alkaloids. By HARRY MANN GORDIN and ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1899, **21**, 231—239).—The authors have applied their iodometric method for the estimation of alkaloids (Abstr., 1898, i, 707) to the assay of nux vomica, belladonna root and leaves, and ipecacuanha root. Emetine octiodide is a dark brown powder, scarcely soluble in benzene, ether, or chloroform, moderately soluble in alcohol, and very readily in a mixture of four parts of alcohol with one part of chloroform. The formula assigned to it is $C_{28}H_{40}N_2O_5,HI,I_7$, corresponding with Lefort and Wurtz's formula for emetine (this Journal, 1877, ii, 628). T. M. L.

Pelosine. By MAX SCHOLTZ (*Arch. Pharm.*, 1899, **237**, 199—200). —The pelosine obtained from *Radix Pareiræ bravæ* by extraction

with water containing sulphuric acid and precipitation with sodium carbonate, is shown to be identical with bebeerine (this vol., i, 92).

C. F. B.

Staphisagroine, a New Alkaloid. By FELIX B. AHRENS (*Ber.*, 1899, **32**, 1581—1584 and 1669—1670).—After the extraction of the alkaloids delphinine, delphinoidene, delphisine, and staphisagrine from the seeds of *Delphinium staphisagria* by means of chloroform, a small quantity of a substance insoluble in this solvent remains behind. This alkaloid, to which the author gives the name *staphisagroine*, $C_{40}H_{46}N_2O_7$, is a faintly yellow, amorphous powder which melts at 275—277°, and is practically insoluble in all the usual solvents ; it dissolves in dilute hydrochloric acid, from which solution it is re-precipitated on adding ammonia. It yields a *picrate* insoluble in hot alcohol, melting and decomposing at 215—216°. The *aurichloride* is yellow, insoluble, and amorphous, darkening at 180°, and remaining unmelted at 275°. The *platinochloride* is light yellow and amorphous, and does not melt at 275°.

An attempt to reprepare the alkaloid by decomposing the platino-chloride with hydrogen sulphide gave rise to another alkaloid, *staphisagroidine*, $C_{40}H_{40}N_2O_4$, a brownish powder which melts at 185° ; the amorphous *aurichloride* remains unmelted at 270°.

Staphisagroine does not give any of the colour reactions character-istic of the delphinium alkaloids. J. F. T.

Pectins. By ÉMILE BOURQUELOT (*Compt. rend.*, 1899, **128**, 1241—1244. Compare Abstr., 1898, i, 607).—Pectins are substances which dissolve in water, forming viscid solutions which resemble those of the gums and mucilages in yielding mucic acid by oxidation with nitric acid, and differ from them in being coagulated by barium and calcium hydroxides and the soluble ferment pectase ; moreover, the pectins yield pectic acid on treatment with potash. The author has isolated pectins from the quince, rose de Provins, and *Cynorrhodon*, and a variety of gooseberry (*Groseille à maquereau*), by extracting the vegetable matter with alcohol, digesting with water at 108—110°, and precipitating the pectin from the aqueous solution by alcohol. The four pectins thus obtained, and that from gentian root are, contrary to Fremy's observation, optically active ; they are all dextrorotatory, the value of a_D varying from 82·3° to 194°. They yield arabinose on hydro-lysis with dilute sulphuric acid, and mucic acid on oxidation with nitric acid ; it appears probable therefore that they are derived in part from araban and galactan, although only in the case of the pectin from gentian has a product resembling galactose been obtained on hydrolysis.

Germinated barley contains a soluble ferment capable of hydrolysing pectins, and as this is absent in the saliva and in the juice of *Aspergillus niger*, it cannot be amylase which occurs in these fluids ; in all probability, it is a new ferment and the name *pectinase* is suggested for it. When pectinase is added to a solution of pectin, the latter is no longer coagulable by pectase and a reducing sugar is produced ; more-over, the ferment has the power of dissolving the coagulum produced by pectase, the action being one of hydrolysis. On adding the two

ferments simultaneously to a solution of pectin, a coagulum appears and afterwards redissolves if the pectase is in excess; if, however, the pectinase predominates, the solution remains clear. The effects of pectase and pectinase on pectins are quite comparable with those of rennet and trypsin on casein; in each case, the former ferment coagulates whilst the latter redissolves the coagulum.   G. T. M.

Pectin Present in Gooseberry. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1899 [vi], **6**, 281—286).—The pectin was obtained from the crushed gooseberries by a method analogous to that employed for the extraction of pectin from gentian root (Abstr., 1898, i, 607). It is completely soluble in water, the solution being dextrogyrate $[a]_D + 194\cdot1^\circ$. A 1 per cent. solution of the pectin is coagulated by a solution of pectase, this occurring more readily if a little precipitated chalk be added; it is also gelatinised by lime water, baryta water, lead acetate, &c.; the sulphates of magnesium and ammonium precipitate it from its solution, but sodium sulphate does not. When heated with nitric acid of sp. gr. 1·15, the pectin yields mucic acid, and when heated under pressure at 105—110° with 2 per cent. sulphuric acid, arabinose is produced. After treatment with malt diastase, the pectin solution is no longer coagulated by a solution of pectase; this change is believed to be due to the action of a ferment present in the diastase for which the name "*pectinase*" is proposed (compare preceding abstract).   H. R. LE S.

Oxidising Ferments in Aconite and Belladonna. By E. LÉPINOIS (*J. Pharm.*, 1899 [vi], **2**, 49—52).—The roots and leaves of aconite and belladonna contain an oxidising ferment (oxydase), which is similar to those studied by Bertrand and others (compare Brissemoret and Joanne, this vol., ii, 319). The ash contains small quantities of iron and manganese. When exposed to air, the ferment absorbs oxygen, and carbonic anhydride is produced.   H. R. le S.

Constitution of the Proteid Molecule. By FR. PRÖSCHER (*Zeit. physiol. Chem.*, 1899, **27**, 114—122).—The products of decomposition of hæmoglobin brought about by hydrochloric acid were estimated, but only about half the nitrogen, carbon, and oxygen and two-thirds of the hydrogen were accounted for.   W. D. H.

The Nitrogen in the Proteid Molecule, By WALTHER HAUSMANN (*Zeit. physiol. Chem.*, 1899, **27**, 95—108).—The differences between different proteids, so far as nutrition is concerned, is associated with a fundamental chemical difference in the way in which their nitrogen is combined, as evinced by the nature of the products of decomposition by acids. These products may, by their chemical behaviour, be divided into three categories, which admit of estimation without separation of the individual constituents, and the nitrogen so obtained may be termed (1) amidic nitrogen, (2) diamino-nitrogen (from diaminoacids, &c., such as lysine, arginine, and histidine), (3) monaminonitrogen (from compounds such as leucine, tyrosine, aspartic and glutamic acids, &c.).

The following table gives the results of determinations made in this manner :—

	Amidic nitrogen, per cent.	Diamino-nitrogen, per cent.	Monamino-nitrogen, per cent.	Total.
Crystallised egg-albumin...	8·53	21·33	67·80	97·66
Crystallised serum-albumin	6·34	—	—	—
Serum-globulin	8·90	24·95	68·28	102·13
Casein	13·37	11·71	75·98	101·06
Gelatin	1·61	35·83	62·56	100·00

W. D. H.

Action of Formaldehyde on Proteids. By CHARLES LEPIERRE (*Compt. rend.*, 1899, **128**, 739—742).—The author has investigated the action of formaldehyde on the heteroalbumoses, protalbumoses, deuteroalbumoses, and peptones prepared by the artificial digestion of egg-albumin, fibrin, muscle, and gelatin. At the ordinary temperature, there is little or no action, but at 100° there is energetic reaction, the substance being precipitated, or being materially changed without becoming insoluble.

Protalbumoses are precipitated by formaldehyde from hot solutions, and the product is insoluble in hot water or in a 10 per cent. sodium chloride solution, or in sodium carbonate solution. Deuteroalbumoses of high molecular weight are precipitated by formaldehyde, whilst those of low molecular weight are converted into protalbumoses, and the latter by further action of the reagent are precipitated. The true peptones are first converted into deuteroalbumoses, and the latter are subsequently changed into protalbumoses in the manner just indicated.

When the products of the action of formaldehyde are heated for an hour or two at 110°, they become hydrated, dissolve completely, and are converted into proteids of the same character as the original substance.

The albumoses and peptones precipitated by formaldehyde are capable of slow digestion by pepsin, and therefore are not, as Trillat supposed, incapable of being assimilated.

It will be seen that the action of formaldehyde is closely analogous to the gradual retrogression of peptones and albumoses to the original proteids of high molecular weight. C. H. B.

Globulin of White of Egg. By ALEXEI A. PANORMOFF (*Chem. Centr.*, 1898, ii, 358; from *J. Russ. Chem. Soc.*, 1898, **29**, 22—27).— Globulin is prepared by diluting fresh white of hen's egg with 1/3—1/4 its volume of water, adding an equal volume of a saturated solution of ammonium sulphate to the filtrate, and leaving the mixture for a month; the precipitate is then pressed between filter paper, and extracted with a half-saturated solution of ammonium sulphate. After a week's exposure in a flat dish, a precipitate consisting of minute needles is formed; these have a specific rotatory power $[a]_D - 23\cdot9°$. A substance crystallising in small needles is also obtained by freezing white of egg and then treating with ammonium sulphate as before

its specific rotatory power is $[a]_D - 24.2°$. Globulin hydrochloride, prepared by dialysing the crystalline globulin into a 0.2 per cent. solution of hydrochloric acid, has the composition $C = 50.80$, $H = 7.392$, $N = 15.13$, $Cl = 2.84$, $S = 1.66$, and a specific rotatory power $[a]_D - 41.8 — 51.9$. The solution obtained by heating for two hours with a 0.2 per cent. solution of hydrochloric acid has a specific rotatory power $[a]_D - 79.56°$, and the precipitate formed from it, by adding alcohol and ether, is easily soluble in hot water, and contains 60.56 C, 6.58 H, 14.65 N, 2.58 Cl, and 1.6 S. The properties and behaviour of the crystalline globulin are identical with those of crystalline albumin, and egg-globulin may be regarded as a mixture of the latter with an unknown compound. E. W. W.

Albumins of White of Egg. By ALEXEI A. PANORMOFF (*Chem. Centr.*, 1898, ii, 487—488; from *J. Russ. Chem. Soc.*, 1898, **30**, 302—310). —Besides the crystalline albumin obtained from white of hen's egg by Hofmeister's method, an amorphous albumin may be separated by fractionally precipitating the solution in saturated ammonium sulphate solution, and fractionally dissolving the precipitate in a half-saturated solution of the sulphate until the product attains a constant specific rotatory power. This albumin (II) separates in globular masses, which become pink at the ordinary temperature and are stable only below 10°; it gives the reactions of white of egg, and has the properties of an acid derivative. When dialysed in ammonium sulphate solution, the specific rotatory power is $[a]_D - 36.2°$, that of the crystalline albumin (I) being 23.6°; and when dialysed in water at 0—5°, it yields a faintly pink, acid solution. The molecular weight is calculated to be 3358. The hydrochloride contains 3HCl, has a specific rotatory power $[a]_D - 54.8°$, is easily soluble in water, and is precipitated by alcohol and ether. When heated in a sealed tube with a 0.1 per cent. solution of hydrochloric acid for $1\frac{1}{4}$ hours, its specific rotatory power increases to $-63.5°$, although its composition remains practically unchanged. The hydrobromide contains 2HBr, and has the specific rotatory power $[a]_D - 53°$, rising to $-63.5°$ when heated with acid. The phosphate contains $5H_3PO_4$ to 2 mols. of albumin, and when dialysed in a 0.2 per cent. solution of phosphoric acid has a specific rotatory power $[a]_D - 52.5°$. White of egg probably only contains the albumins (I) and (II), for the specific rotatory powers of the hydrochlorides, hydrobromides, and phosphates, prepared directly from it, correspond within limits of errors of experiment with the mean of the values obtained for the corresponding compound of each albumin. E. W. W.

Action of Dilute Solutions of Pyrophosphoric Acid on the Crystalline Albumin of White of Egg. By WLADIMIR WORMS (*Chem. Centr.*, 1898, ii, 488; from *J. Russ. Chem. Soc.*, 1898, **30**, 310—319).—Preparations of the crystalline albumin (I) of white of egg, freed from ammonium sulphate by dialysing into water, were treated with pyrophosphoric acid until the acid reaction was shown with tropæolin OO and were then dialysed into 0.05, 0.2, and 0.5 per cent. solutions of pyrophosphoric acid. The three solutions showed the same properties and had the specific rotatory power $[a]_D - 26.1°$,

but since the precipitates obtained by adding 95 per cent. alcohol to the more concentrated solutions of pyrophosphoric acid have a greater content of phosphorus, this acid, like orthophosphoric acid, probably forms several different compounds with the albumin. When the solutions of the albumin pyrophosphates are heated in a closed tube at 100°, the properties of the liquids, and the composition of the precipitates obtained from these by adding alcohol and ether, show that the pyrophosphates have become orthophosphates, although the specific rotatory power of the precipitates is $[\alpha]_D - 67\cdot5°$, whilst that of the corresponding orthophosphates is $-58\cdot8°$. E. W. W.

Products of the Action of Pepsin and Pancreatic Juice on Fibrin. By V. HARLAY (*J. Pharm.*, 1899, [vi], 5, 225—232).— The digestive action of pepsin or pancreatic juice on fibrin has, until now, been regarded as ended when the filtered liquid gives no turbidity with nitric acid ; this is shown to be incorrect, as by continuing the digestion beyond this stage, tyrosine crystals were obtained, and the rotatory power of the solution was found to go on diminishing in value. The colour change from red to black produced by the juice of *Russula delica* is characteristic of tyrosine, and is given by the solution obtained by the action of pepsin on fibrin, whereas a red coloration changing to green is produced if the fibrin is digested with pancreatic juice. H. R. LE S.

Organic Chemistry.

Chemical Action of the Silent Electric Discharge on Carbon Compounds. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1899, [vii], 16, 5—103).—A detailed account of work already published (compare Abstr., 1897, i, 330; 1898, i, 393, 551, 554, 558, and 594).
<div align="right">G. T. M.</div>

Conversion of Trimethylene into Propylene. By SIMEON M. TANATAR (*Ber.*, 1899, 32, 1965—1967. Compare Abstr., 1896, i, 457, and this vol., i, 422).—When a mixture of trimethylene and propylene is rapidly (6—7 litres per hour) bubbled through well-cooled bromine, practically the whole of the trimethylene passes through unaltered, whilst the propylene is completely absorbed, forming propylenic bromide. This difference affords an easy method for the complete conversion of trimethylene into propylene. The trimethylene is passed through a hot tube and then through bromine, the unabsorbed gas is passed through the hot tube again and then through the bromine, and these processes are repeated until practically the whole of the gas is absorbed. A control experiment proved that trimethylene itself, when passed through bromine, does not yield propylenic bromide.
<div align="right">J. J. S.</div>

Absorption of Hydrogen Phosphide in Presence of Alkali Chlorides and the Purification of Crude Acetylene. By CHRISTIAN GÖTTIG (*Ber.*, 1899, 32, 1879—1882).—On passing acetylene containing hydrogen phosphide into an aqueous solution of a mixture of cupric chloride with an alkali chloride, copper phosphide, Cu_6P_2, is formed, but the precipitation of copper acetylide is not prevented. The presence of an alkali chloride, however, prevents a solution of mercuric chloride from uniting with acetylene to form an explosive compound, although its power of absorbing hydrogen phosphide is increased; during this absorption, a white substance separates which probably consists of mercury phosphide, combined with mercuric phosphate, and there is also formed a yellow compound, $3Hg_3P_2,7HgCl_2$, a red compound, $4Hg_3P_2,HgCl_2$, and a brown compound, $Hg_3P_2,HgCl_2$.

The conclusion is drawn that the absorption of hydrogen phosphide present in acetylene by solutions of easily reducible metallic salts is increased by the presence of a chloride of an alkali metal, whilst the need of using acids to prevent the formation of explosive metallic compounds of acetylene is obviated.
<div align="right">W. A. D.</div>

Copper Acetylide. By MARTIN FREUND and LUDWIG MAI (*Chem. Centr.*, 1899, i, 410—411; from *Acetylen in Wiss. u. Ind.*, 1898, 285—286).—When copper acetylide dried at 50—60° is placed in a tube through which acetylene is passed, it explodes after a short time, but does not cause the explosion of the acetylene. The copper acetylide is itself only explosive when it has been exposed to the action of oxygen or air in the process of drying.
<div align="right">E. W. W.</div>

Allene Hydrocarbons. By WLADIMIR IPATIEFF (*J. pr. Chem.*, 1899, [ii], 59, 517—542).—The allene hydrocarbons are prepared by

the action of alcoholic potash on the corresponding keto-dichlorides. β-*Diethylallene*, $CEt_2:C:CH_2$, prepared from the chloride derived from diethylacetone, is a colourless, strongly refractive liquid which boils at 96—98°, and has a sp. gr. 0·7475 at 0°/0°. On treatment with hydrogen bromide in acetic acid solution, it gives a-*bromo-γ-ethylpentylene*, $CEt_2:CH \cdot CH_2Br$, which boils at 152—154°, has a sp. gr. 1·2079 at 0°/0°; and aγ-*dibromo-γ-ethylpentane*, $CBrEt_2 \cdot CH_2 \cdot CH_2Br$, boiling at 109—110°, and of sp. gr. 1·5799 at 0°/0°. By the action of alcoholic potash on the latter, there are obtained β-diethylallene and *ethylic* β-*diethylallylic ether*, $CEt_2:CH \cdot CH_2 \cdot OEt$, which boils at 156—158°, and has a sp. gr. 0·8290 at 0°/0°.

β-*Methylethylallene*, $CMeEt:C:CH_2$, prepared from the chloride of methylethylacetone, is a very strongly refractive, transparent liquid boiling at 70—71°, and of sp. gr. 0·7310 at 0°/0°. With hydrogen bromide, it gives aγ-dibromo-γ-methylpentane, $CMeEtBr \cdot CH_2 \cdot CH_2Br$, which boils at 94—96°, and has a sp. gr. 1·6360 at 0°/0°. On treatment with alcoholic potash, this compound is converted into β-methylethylallene and *ethylic* β-*methylethyl allylic ether*; the latter boils at 141—143°, and has a sp. gr. 0·8208 at 0°/0°.

By the action of alcoholic potash on trimethyltrimethylenic dibromide, $CMe_2Br \cdot CH_2 \cdot CHMeBr$, an unsaturated *ether* is obtained, probably having the formula $CMe_2:CH \cdot CHMe \cdot OEt$, which boils at 124—126°, and has a sp. gr. 0·8084 at 0°/0°.

The various allene hydrocarbons can be distinguished by treatment with hydrogen bromide and subsequently with alcoholic potash: (i) Mono-substituted allenes give dibromotrimethylenes (compare Ipatieff, Abstr., 1896, i, 330), $R \cdot CH:C:CH_2 + 2HBr = R \cdot CHBr \cdot CH_2 \cdot CH_2Br$. These, with alcoholic potash, give unsaturated primary mono-substituted ethylic allylic ethers, $R \cdot CHBr \cdot CH_2 \cdot CH_2Br \longrightarrow R \cdot CH:CH \cdot CH_2 \cdot OEt$; (ii) β-di-substituted allenes give β-di-substituted dibromotrimethylenes $CR_2Br \cdot CH_2 \cdot CH_2Br$, from which unsaturated primary β-di-substituted ethylic allylic ethers, $CR_2:CH \cdot CH_2 \cdot OEt$, can be obtained; (iii) tri-substituted allenes give tri-substituted dibromotrimethylenes, $CR_2Br \cdot CH_2 \cdot CHRBr$, which yield unsaturated secondary tri-substituted ethylic allylic ethers, $CR_2:CH \cdot CHR \cdot OEt$; (iv) tetra-substituted allenes give tetra-substituted dibromotrimethylenes, $CR_2Br \cdot CH_2 \cdot CBrR_2$, which, with alcoholic potash, yield the original hydrocarbon.   R. H. P.

Formation of Cuprous Cyanide. By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 261—262).—By heating a mixture of copper acetate and aqueous ammonia for two hours in a sealed tube at 180—185°, a colourless liquid is obtained containing in suspension finely divided copper and a white precipitate consisting of crystalline plates. On filtering the liquid, which immediately turns blue, and removing the copper from the precipitate by digesting it with very dilute sulphuric acid, the residual crystalline plates are found to consist of cuprous cyanide. On mixing the blue filtrate with alcohol and placing it in a desiccator, blue needles of copper carbonate are deposited.   T. H. P.

Substituted Cyanamides and Thiocarbamides. By OTTO WALLACH (*Ber.*, 1899, 32, 1872—1875).—The following di-substituted

cyanamides have been prepared by the action of cyanogen bromide (1 mol.) on an ethereal solution of the secondary amine (2 mols.). *Cyanodimethylamine*, $CN \cdot NMe_2$, is an oil boiling at 52° under 14 mm. pressure. *Cyanodiethylamine*, $CN \cdot NEt_2$, is an oil boiling at 68° under 10 mm. pressure. *Cyanodipropylamine*, $CN \cdot NPr_2$, is an oil boiling at 88—90° under 10 mm. pressure. *Cyanodiamylamine*, $CN \cdot N(C_5H_{11})_2$, is an oil boiling at 130—132° under 10 mm. pressure. *Cyanopiperidine*, $CN \cdot C_5NH_{10}$, is an oil boiling at 102° under 10 mm. pressure. *Cyanodibenzylamine*, $CN \cdot N(CH_2Ph)_2$, melts at 54° and boils at 145—148° under 10 mm. pressure. *Cyanomethylaniline*, $CN \cdot NMePh$, melts at 28° and boils at 136° under 10 mm. pressure. Unlike cyanamide and the monalkylcyanamides, these substances have no tendency to polymerise. By saturating an alcoholic solution with ammonia and hydrogen sulphide, they are converted into the corresponding thiocarbamides, some of which have already been prepared by isomeric change from the thiocyanates, as is shown in the following table :

Base.		Melting point.	
$NH_2 \cdot CS \cdot NMe_2$	158—159°	{	159° H. Salkowski.
			81— 82° Spica and Carrara.
$NH_2 \cdot CS \cdot NEt_2$	101—102	169—170° Spica and Carrara.	
$NH_2 \cdot CS \cdot NPr_2$	67	—	
$NH_2 \cdot CS \cdot N(C_5H_{11})_2$	63—64	208—209° Spica and Carrara.	
$NH_2 \cdot CS \cdot NC_5H_{10}$	128		
$NH_2 \cdot CS \cdot N(CH_2Ph)_2$	139—140	139—140° H. Salkowski.	
$NH_2 \cdot CS \cdot NMePh$	106—107	107° Gebhardt.	

T. M. L.

Etherification of Phosphoric Acid by the Aid of Methylic Alcohol. By GUILLAME BELUGOU (*Bull. Soc. Chim.*, 1899, [iii], **21**, 166—169).—The conclusions arrived at are :—(1) That by the action of phosphoric acid on methylic alcohol the limit of etherification is instantaneously reached, and that this limit is independent of the manner in which the acid and alcohol are mixed. (2) That an increase in temperature or time serves to diminish the coefficient of etherification until it reaches a minimum of about 10 per cent., when it gradually increases again. (3) That the presence of minute quantities of water diminishes the rate of etherification to a very appreciable extent. Preliminary experiments proved that the product is a monomethylic phosphate. J. J. S.

Behaviour of Isomeric Alcohols with Phosphorus Trichloride. By TH. MILOBENDSKI (*Chem. Centr.*, 1899, i, 249; from *J. Russ. Chem. Soc.*, 1898, **30**, 730—734).—According to Jaroschenko (*ibid.*, **29**, 223), by the action of phosphorus trichloride on secondary alcohols, olefines, and sometimes small quantities of alkylic chlorides, are formed. The author finds, however, that by the action of phosphorus trichloride on isopropylic alcohol, di-isopropylic phosphite, isopropylic chloride, hydrogen chloride, and a very small quantity of propylene are obtained. The product of the reaction, when distilled under the

ordinary pressure, yields only isopropylic chloride. *Di-isopropylic phosphite*, $P(OPr)_2OH$, is a limpid liquid, boils at 72—73° under 6·5 mm., at 76—77° under 10 mm., and at 85—86° under 17 mm. pressure. The silver salt, prepared by means of a concentrated solution of silver nitrate containing a few drops of ammonia, is a white, amorphous substance. E. W. W.

Preparation of Ethylenic Glycol. By Louis Henry (*Rec. Trav. Chim.*, 1899, 18, 221—227).—When powdered caustic potash is added to glycol diacetate, rapid action occurs, and on distilling under reduced pressure, a 90 per cent. yield of glycol is obtained ; an equally good yield of propylenic glycol can be obtained in similar manner from its acetate. Since the potassium acetate, formed in these cases, fuses during distillation and frothing occurs, the method is improved by using baryta or, better, dry powdered calcium hydroxide to effect the hydrolysis ; under these conditions, no frothing occurs during distillation and the yield is 93 per cent. of the theoretical. W. A. D.

Oxidation of Trichlorethoxyethylene. By Louis Henry (*Rec. Trav. Chim.*, 1899, 18, 215—220).—When trichlorethoxyethylene, $CCl_2{:}CCl{\cdot}OEt$, is exposed to moist air, it is converted into oxalic acid, hydrogen chloride being evolved ; the same is true of the corresponding trichloromethoxyethylene. On passing a stream of dry oxygen, however, over trichlorethoxyethylene, it is converted into a colourless, fuming liquid, which the author has previously assumed to be dichlorethoxyacetic chloride, $OEt{\cdot}CCl_2{\cdot}COCl$ (Abstr., 1879, 231). When distilled, under atmospheric pressure, the larger part of this substance passes over at 140°, although portions distil between 100° and 140°, and 140° and 200°. Since the compound, $OEt{\cdot}CCl_2{\cdot}COOEt$, obtained by acting on ethylic oxalate with phosphorus pentachloride (Anschütz, Abstr., 1890, 236), boils, under atmospheric pressure, at the same temperature as ethylic oxalate, the author concludes that the compound $OEt{\cdot}CCl_2{\cdot}COCl$ would have approximately the same boiling point, about 140°, as ethyloxalic chloride, $COOEt{\cdot}COCl$, and his former assumption as to the nature of the oxidation product of trichlorethoxyethylene is justified. It is probable that the portion which distils below 140° consists largely of oxalic chloride, formed by the decomposition of dichlorethoxyacetic chloride ; whilst the fraction boiling above 140° probably contains ethylic hydrogen oxalate, formed by moisture present in the oxygen acting on the original trichlorethoxyethylene. The author intends returning to the subject. W. A. D.

Glycerophosphoric Acid. By Jacques Cavalier and Pouget (*Bull. Soc. Chim.*, 1899, [iii], 21, 364—366).—Calcium glycerophosphate, like the alkaline earth salts of the various monalkylphosphoric acids, is less soluble in hot than in cold water. The weight of the anhydrous salt contained in 100 grams of the saturated aqueous solution was found to be 7·9 grams at 16°, 4·4 grams at 36°, 2·3 grams at 51°, 1·3 grams at 77°, 1·25 grams at 86°, and 1·15 grams at 100°. On boiling the cold, saturated solution, the greater part of the salt is deposited, and its purification is better effected by this means than by precipitation with alcohol. Calcium glycerophosphate is comparable as regards

stability with calcium ethyl- and methyl-phosphates, a hot, saturated solution of the salt acquiring only a slight opalescence when heated at 95° for 3 hours. The barium salt is less stable, and on this account, and also because its solubility varies less with the temperature, its purification is better effected by precipitation with alcohol. At the ordinary temperature, a saturated solution contains 4·5 per cent. of the salt, which is reduced to 3 per cent. on boiling.

Glycerophosphoric acid, in presence of phosphoric acid, may be estimated by the process previously described (this vol., ii, 55) for the estimation of alkyl phosphates, but the results are not quite so satisfactory as in the latter case. The hydrolysis of the acid, which was studied in the case of a 0·1 normal solution at 88°, obeys the law for monomolecular reactions, and the velocity of decomposition increases rapidly with rise of temperature. Comparison of the value (0·0058) found for k in the equation $x = e^{-kt}$, that is, for the amount of acid decomposed in one hour under the above conditions, with the corresponding values for methylphosphoric (0·0056), ethylphosphoric (0·0032), and allylphosphoric (0·0055) acids shows that the stability of glycerophosphoric acid is much less than that of ethylphosphoric acid but practically equal to that of methyl- and allyl-phosphoric acids.   N. L.

Action of Alkalis on the Sugars. VI. Maltose, Lactose, and Melibiose. By CORNELIS A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1899, 18, 147—149. Compare Abstr., 1898, i, 225 and 227).—When a 20 per cent. aqueous solution of maltose is heated with one-fifth its volume of normal caustic potash for 3 hours at 100°, dextrose is initially formed, but undergoes conversion into mannose, which can be isolated in the form of its phenylhydrazone. On fermenting the solution, a residue remains which has a dextrorotatory power nearly one-half that of dextrose; this residue, which is converted into dextrose by the action of dilute acid, and thus rendered fermentable, appears to consist of an anhydride of dextrose.

Lactose, on treatment with alkali, yields galactose, which can be isolated in the form of its phenylmethylhydrazone; a small quantity of ψ-tagatose is also formed, but neither dextrose nor mannose can be isolated; dextrose, if formed, appears to exist as anhydride. Lead hydroxide converts lactose into the same products as caustic potash.

Melibiose, under the influence of potash or lead hydroxide, yields galactose; the formation of dextrose could not be proved.

Fischer has shown that the aldehyde-group of lactose is in that portion of the molecule which, on inversion, yields dextrose; the authors' experiments indicate, on the contrary, that this group is in the portion which gives rise to galactose. The apparent contradiction awaits explanation.   W. A. D.

Compounds Formed by Polyhydric Alcohols with Benz-aldehyde. By CORNELIS A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1899, 18, 150—152).—The following table gives the properties of the products formed by the condensation of certain polyhydric alcohols with benzaldehyde.

Name.	Melting point. °F.	Specific rotatory power [α]_D			Solubility (milligrams) in 10 c.c. at 16—18°.			Completely decomposed after boiling with 20 times its weight of normal H_2SO_4 for
		for 0·25—0·5 per cent. solutions.	of the free alcohols (0·5 per cent.) with ammonium molybdate.		Acetone.	Chloroform.	Alcohol.	
			6·75/24 mol.	After adding 2 c.c. normal H_2SO_4 per 25 c.c.				
Dibenzylidene-erythritol	201°	0° (chloroform)	0°	0°	34	364	2	—
Monobenzylidenearabitol......	152	0 ,,	−42	−94	—	—	—	—
Dibenzylideneadonitol	165	0 ,,	0	0	64	136	14	—
Dibenzylidenexylitol	175	0 ,,	—	—	110	85	—	—
Dibenzylidenerhamnitol	203	−55 ,,	−43	−115	70	255	110	1½ hours
Monobenzylidene-d-sorbitol...	175	+6 (alcohol)	—	—	very	easily	soluble	—
Dibenzylidene-d-sorbitol......	163	+29 (acetone)	+41	+90	544	16	10	½ hour
Tribenzylidenemannitol......	213—218	−13 (chloroform)	+43	+120	42	875	10	8 hours
Tribenzylidene-l-iditol*	215—218	−6 (acetone)	+107	+37	47	17	5	2 hours
Tribenzylidene-d-talitol†	210	−40 (chloroform)	+60	+8	30	442	traces	6 hours
Dibenzylidenedulcitol	215—220	0 ,,	0	—	42	83	traces	—
Dibenzylideneperseitol.........	230—235	−60 (acetone)	+48	+132	4	traces	2	—

* Prepared from l-idonic acid.　　　　† Prepared from d-talonic acid.

W. A. D.

Action of Aqua Regia on Fatty Primary Amines. By WASSILY A. SOLONINA (*Chem. Centr.*, 1899, i, 254; from *J. Russ. Chem. Soc.*, 1898, **30**, 822—825).—By the action of a mixture of 4 parts of hydrochloric acid of sp. gr. 1·16 with 1—1½ of nitric acid of sp. gr. 1·4 on salts of hexamethylenediamine, dichlorohexane and a compound containing more chlorine were obtained, and the pro-duct of the reaction, when treated with sodium phenoxide, yielded *aa'*-diphenoxyhexane melting at 82·5° and other substances which were not identified. Salts of octomethylenediamine with aqua regia also form chlorine compounds, and by treating the product with sodium phenoxide *aa'*-diphenoxyoctane was prepared. By the action of aqua regia on benzylamine and isobutylamine, benzylic and isobutylic chlorides were respectively obtained, together with other liquid and solid products. E. W. W.

Composition of Nitrogen Iodide and the Action of Iodine on Fatty Amines. By JAMES F. NORRIS and ARTHUR I. FRANKLIN (*Amer. Chem. J.*, 1899, **21**, 499—509. Compare Chattaway, Trans., 1898, **69**, 1572).—On mixing ethereal solutions of iodine and triethyl-amine at ordinary temperatures or at $-3°$, an oil separated which had the composition of a *periodide*, $NHEt_3I,I_2$, and yielded hydrogen iodide when treated with concentrated sulphuric acid; the mother liquor contained triethylamine hydriodide; similar results were obtained when carbon tetrachloride was used as the solvent. In dilute aqueous solution, iodoform was precipitated, but in concentrated solution, the oily periodide was formed. No indication was observed of the forma-tion of an additive product, NEt_3I_2, comparable to those obtained from trimethylamine and tripropylamine.

On mixing ethereal solutions of tripropylamine and iodine, an oil was obtained which gradually deposited stout, prismatic crystals of the *iodide* NPr_3I_2; these melted at 66°, and were not acted on by con-centrated sulphuric acid; the compound is insoluble in ether, slightly soluble in carbon tetrachloride, soluble in ethylic acetate or chloroform, and in contact with water melts to an oil. With carbon tetrachloride as solvent, an oil was obtained together with crystals of tripropylamine hydriodide. In aqueous solution, an oil was precipitated having the composition of the *periodide*, $NHPr_3I,I_2$.

On mixing ethereal solutions of diethylamine and iodine, a dark oil was precipitated which yielded hydrogen iodide when treated with sulphuric acid, and was therefore not a direct additive product; diethylamine hydriodide is also formed. Similar results were obtained with carbon tetrachloride as a solvent; in dilute aqueous solution, in presence of sodium carbonate, iodoform was produced; in the absence of any solvent, a violent reaction takes place, accompanied by much heat and the evolution of white fumes, but at $-18°$ the two substances were inactive.

On mixing ethereal solutions of diamylamine and iodine, a black, crystalline *periodide*, $NH_2(C_5H_{11})_2I,I_2$, is precipitated; this can also be prepared by mixing diamylamine hydriodide and a solution of iodine in hydriodic acid.

On passing methylamine into an ethereal solution of iodine, a black, crystalline *periodide* is precipitated; on adding a solution of iodine in

carbon tetrachloride to a solution of methylamine in the same solvent, methylamine hydriodide is produced, but no additive product.

The non-explosive oil prepared by Guthrie (this Journal, 1863, **16**, 239) by adding powdered iodine to a saturated solution of an easily soluble ammonium salt partially decomposed by one-third its equivalent of potassium hydroxide, and by Seamon (Abstr., 1882, 8), by passing ammonia over iodine at 0°, is shown to be similar in all respects to the oil obtained by dissolving nitrogen iodide in ammonium periodide; the mixture dissolves readily in ether, although nitrogen iodide is itself insoluble in ether.

In conclusion, the author states that iodine readily attacks all fatty amines, giving an unstable substitution product and liberating hydrogen iodide, which combines with the amine to form a hydriodide; in aqueous solutions, iodoform appears as an extreme substitution product. An additive compound, NR_3I_2, is only formed in the case of tertiary amines, and even then substitution also takes place. He therefore concludes that nitrogen iodide is not an additive compound, NH_3,I_2, as assumed by Chattaway, but a substitution product.

<div align="right">T. M. L.</div>

NOTE.—Chattaway has been led by further investigation to the formula $N_2H_3I_3$ for nitrogen iodide, and regards it as a substitution derivative (Proc., 1899, 17—20).—EDITORS.

Amines and Amides derived from Aldehydes. By MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1899, [vii], **16**, 103—115; 221—274). —A *résumé* of work already published (compare Abstr., 1898, i, 363, 415, 462; ii, 368, 501, 559; this vol., i, 186, 234, 326, 410, 414), including details of methods of preparation and tables of thermochemical data.

<div align="right">G. T. M.</div>

Secondary Bases from Ethylenediamine. By LEOPOLD BLEIER (*Ber.*, 1899, **32**, 1825—1830).—By the action of trimethylenic bromide on ethylenediamine, a product, probably a mixture of ethylenediamine hydrobromide and trimethylene-ethylenediamine hydrobromide, was obtained, which could not be further purified.

Trimethylene-ethylenedibenzenesulphonamide,

$$\begin{array}{c} CH_2 \cdot N(SO_2Ph) \cdot CH_2 \\ CH_2 \cdot N(SO_2Ph) \cdot CH_2 \end{array} > CH_2,$$
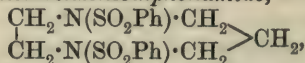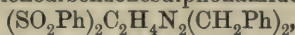
obtained by the action of benzenesulphonic chloride (2 mols.) on ethylenediamine (1 mol.) in the presence of an excess of sodium hydroxide solution, crystallises in glistening plates and melts at 148—149°; when hydrolysed with concentrated hydrochloric acid at 150—160°, it yields *trimethylene-ethylenediamine hydrochloride,* $C_2H_3 \cdot N_2H_2 \cdot C_3H_6,2HCl$ which crystallises from alcohol in thin, colourless, extremely hygroscopic needles. The *base,* $C_5H_{12}N_2$, distils at 168—170°, and then sets to a mass of glistening, colourless crystals; it fumes in the air, is extremely deliquescent, and its aqueous solution has a strongly alkaline reaction; although readily soluble in alcohol or chloroform, the base is only sparingly soluble in ether. The *hydrobromide* crystallises in glistening plates, is extremely hygroscopic, and turns black at 220° without melting; the *platinochloride,* $C_5H_{12}N_2,H_2PtCl_6$, crystallises in orange-yellow plates, turns black

at $270°$, and melts and decomposes at $292°$. The *aurichloride*, $C_5H_{12}N_2(HAuCl_4)_2$, forms a pale, yellow precipitate; the *mercurichloride*, $C_5H_{12}N_2,2HCl,4HgCl_2$, is colourless, melts at $243°$, and is soluble in hot water; the *picrate*, $C_5H_{12}N_2,2C_6H_3N_3O_7$, crystallises in short, yellow needles which turn black at $240°$ and melt and decompose at $265°$. The *dinitroso*-derivative, $C_5H_{10}N_2(NO)_2$, melts at $92°$, and is only sparingly soluble in light petroleum; the *dibenzoyl* derivative, $C_5H_{10}N_2Bz_2$, crystallises in glistening lamellæ containing water of crystallisation, it loses this at $103°$ and then melts at $108°$.

Benzylic chloride also reacts with ethylenedibenzenesulphonamide, yielding dibenzylethylenedibenzenesulphonamide,
$$(SO_2Ph)_2C_2H_4N_2(CH_2Ph)_2,$$
which crystallises from acetic acid in felted needles melting at $220°$. When hydrolysed with concentrated hydrochloric acid at $170—180°$, it yields *dibenzylethylenediamine hydrochloride* which does not melt at $270°$. *Monobenzylethylenediamine*, $C_2H_7N_2 \cdot CH_2Ph$, may also be obtained by hydrolysing the disulphonamide with concentrated hydrochloric acid; it boils at $162—165°$ under 20 mm. pressure, and rapidly turns yellow on exposure to the atmosphere; its *hydrochloride* crystallises in large, thin plates melting at $253°$; the *aurichloride* crystallises in slender needles decomposing above $230°$; the *mercurichloride* $C_2H_7N_2 \cdot CH_2Ph,2HCl,2HgCl_2$, forms small, glistening plates, melting at about $263°$, and the *picrate*, pale yellow plates or slender needles, melting and decomposing at $222°$.   J. J. S.

Occurrence of Acetaldehyde in Petroleum Products. By CLARENCE J. ROBINSON (*J. Soc. Chem. Ind.*, 1899, **18**, 232).—Water which has been in contact with the lighter products from petroleum may contain a small quantity of acetaldehyde. The amount in crude petroleum may be roughly estimated by agitating the sample with water, or, better still, by first distilling off the naphtha and treating this with water; the amount obtained was about $0·001$ per cent.

On examining the distillates obtained from crude petroleum, it was found that acetaldehyde is present in the light naphtha first obtained, is practically absent from the heavier products immediately following, and that it again appears and reaches a maximum when the temperature of the still is high enough to produce "cracking."   L. DE K.

Formation of Acetals of Glycol. By ALBERT VERLEY (*Bull. Soc. Chim.*, 1899, [iii], **21**, 275—277).—The methylene derivative of glycol, $CH_2{<}^O_O{>}C_2H_4$, obtained by Trillat and Cambier (Abstr., 1894, i, 487) by the action of dry trioxymethylene on glycol in presence of a trace of ferric chloride, can be readily prepared by heating a mixture of glycol, 40 per cent. formaldehyde, and syrupy phosphoric acid for a few minutes on the water-bath; on distilling in a current of steam, a product is obtained which boils at $78°$.

The ethylidene derivative of glycol may be obtained by heating on the water-bath a mixture of glycol and acetaldehyde, in molecular proportion, with syrupy phosphoric acid and a little water; the excess of the aldehyde is dissolved out by means of sodium hydrogen sulphite solution and the liquor rectified.

The *isobutylidene* derivative of glycol, $CHMe_2 \cdot CH{<}^O_O{>}C_2H_4$, is prepared by heating on a water-bath molecular proportions of glycol and isobutaldehyde with a little water and sufficient syrupy phosphoric acid to give a limpid solution ; it is a very mobile liquid, having an unpleasant ethereal odour, boils at 122—123°, and has a sp. gr. 0·9459 at 15°.

The *methylene* derivative of *monochlorhydrin*, $CH_2{<}^{O \cdot CH \cdot CH_2Cl}_{O \cdot CH_2}$, obtained by distilling a mixture of the monochlorhydrin, 40 per cent. formaldehyde, and phosphoric acid on an oil-bath, is a mobile liquid with an odour resembling that of rum, boils at 126° under 750 mm. pressure, and has a sp. gr. 1·279 at 0°.   T. H. P.

Detection and Isolation of Ketones and Aldehydes. By EUGEN BAMBERGER (*Ber.*, 1899, **32**, 1806—1807. Compare Bamberger and Kraus, Abstr., 1896, i, 610).—Paranitrophenylhydrazine is strongly recommended as a reagent for aldehydes and ketones, as the hydrazones thus formed crystallise well, and are neither too readily nor too sparingly soluble. Many of the paranitrophenylhydrazones are so markedly acidic that they dissolve in aqueous solutions of alkalis, but many of the alkali salts thus formed are so strongly hydrolysed in aqueous solution, that their characteristic colours only become visible on the addition of alcohol. Extremely dilute aqueous solutions of acetone or of formaldehyde readily react with paranitrophenylhydrazine. *Formaldehydeparanitrophenylhydrazone* crystallises from cold benzene in glistening, yellow needles melting at 181—182°, and is, in contradistinction to the phenylhydrazone, normally constituted (compare Abstr., 1896, i, 543).

Paranitrophenylhydrazine can be kept for years without decomposition ensuing, whereas the parabromo-compound recommended by Fischer (Abstr., 1892, 439) decomposes when kept for several months.

J. J. S.

Separation of Methyl Ethyl Ketone from Ethylic Alcohol. By R. DUCHEMIN (*Bull. Soc. Chim.*, 1899, [iii], **21**, 314—315).—The use of methyl ethyl ketone for the denaturing of spirits has been suggested by A. and P. Buisine (Abstr., 1898, i, 352), both from the low price and from the difficulty of recovering the alcohol. To 95 per cent. alcohol denatured by the addition of 1/50 of methyl ethyl ketone, the author added quicklime mixed with water and bleaching powder, the whole being kept cool during mixing to prevent the alcohol being attacked. After about 2 hours, the spirit was filtered and rectified in a Le Bel-Henninger tube with three bulbs ; 95 per cent. of the alcohol was recovered, and the spirit thus obtained was of good flavour, and had no unpleasant smell. From this it is concluded that the use of methyl ethyl ketone for denaturing spirit is not to be recommended.

The alcohol can also be recovered from spirits mixed with methyl ethyl ketone by the addition of tartaric acid, yielding ethyltartaric acid, which can be crystallised out and purified by pressing between filter papers ; on dissolving in water and boiling the solution with potash, almost the whole of the alcohol is obtained free from the ketone.

The ketone can also be destroyed by electrolysis.   T. H. P.

Condensing Action of Potassium Cyanide on Aldehydes and on Mixtures of Aldehydes and Ketones. By LUDWIG CLAISEN (*Annalen*, 1899, **306**, 322—331. Compare Abstr., 1893, i, 8).—Since the appearance of the author's first communication (*loc. cit.*), the condensing action of potassium cyanide has been investigated by Kohn (this vol., i, 328). Particulars are now given relating to the preparation of aldol, hydracetylacetone, ethylideneacetone, and isobutaldol cyanhydrin. M. O. F.

A Ketopseudonitrole. By GIACOMO PONZIO (*J. pr. Chem.*, 1899, [ii], **59**, 493—496).—When nitric peroxide (3 mols.) acts on a cold ethereal solution of isonitrosomethyl propyl ketone (4 mols.), crystals of *amylketopseudonitrole*, $COMe \cdot CEt:N_2O_3$, are slowly deposited; it forms unstable, white prisms, melts at 64° to a blue liquid, and decomposes at 65°. It is decomposed on warming or by the continued action of nitric peroxide into methyl ethyl diketone and acetyldinitropropane, and is hydrolysed by dilute potash into acetic and propylnitrolic acids.

Propylnitrolic acid forms long, yellowish needles with a sweet taste, melting at 66° (not at 60°; V. Meyer, Abstr., 1875, 588). R. H. P.

Preparation of Glycocine. By VICTOR AUGER (*Bull. Soc. Chim.*, 1899, [iii], **21**, 5—7).—An aqueous solution of monochloracetic acid is saturated with potassium carbonate and mixed with a solution containing slight excess of hexamethylenetetramine ; the mixture becomes warm and is evaporated to dryness, preferably in a vacuum. The residue, which consists of the compound $C_6H_{12}N_4,CH_2Cl \cdot COOK$, is decomposed by treatment with alcoholic hydrogen chloride; the hydrochloride of ethylic amidoacetate is separated by washing the viscous product with 95 per cent. alcohol, evaporating the filtrate to dryness, treating the residue with calcium carbonate and moist copper oxide, and purifying the copper salt in the usual way. The crude product obtained by extraction may, however, be employed in the preparation of ethylic diazoacetate without further purification. The formal which is also produced by the action of alcoholic hydrochloric acid is reconverted into hexamethylenetetramine by treatment with ammonia. G. T. M.

Electrolysis of $\alpha\alpha\beta$-Trichlorobutyric Acid. By JULIUS TROEGER and ERICH EWERS (*J. pr. Chem.*, 1899, [ii], **59**, 464—469. Compare this vol., i, 12).—Sodium $\alpha\alpha\beta$-trichlorobutyrate was electrolysed, using electrodes of spirally rolled platinum foil with an E.M.F. of 16 volts, and a current varying from 0·3 to 0·5 ampère. Carbonic oxide and an unstable oily product were formed at the anode ; this oil seemingly has the composition $C_2Cl_4(CHMe \cdot OH)_2$, and is probably derived from the action of the sodium hydroxide formed in the electrolysis on the primary product, $C_2Cl_4(CHMeCl)_2$, of the reaction. R. H. P.

[Synthesis of Normal Ethereal Salts of Glycerol and Fatty Acids.] By L. T. C. SCHEIJ (*Rec. Trav. Chim.*, 1899, **18**, 169—210). —The normal ethereal salts were prepared by heating, at a temperature in no case exceeding 200°, a mixture of glycerol and the fatty acid in a distilling flask under considerably diminished pressure ; a slow

Table I.—*Fatty Acids.*

Acid.	Melting point.	Temperature ($t°$) at which density and μ were determined.	Density at $t°$, referred to water at 4°.	Mol. vol. at $t°$.	μ_D at $t°$.	Molecular refraction.	Difference for 2CH₂. Mean for 2CH₂ = 9·34.
Butyric	− 6·5°	20°	0·9590	91·81	1·39906	22·21	9·22
Caproic	− 8·0	20	0·9274	125·16	1·41635	31·43	9·33
Caprylic	16	20	0·9100	158·35	1·42825	40·76	9·29
Capric	31·1	40	0·8858	194·31	1·42855	50·05	9·37
Lauric	43·4—43·6	60	0·8642	231·59	1·42665	59·42	9·35
Myristic	53·6	60	0·8584	265·81	1·43075	68·77	9·41
Palmitic	62·6	80	0·8412	304·56	1·42693	78·18	9·38
Stearic	69·2	80	0·8386	338·92	1·43003	87·56	

Table II.—*Ethereal Salts.*

Name.	Melting point.	Density, referred to water at 4°, at 20°.	40°.	60°.	80°.	$t°$.	Mol. vol. at $t°$. Found.	Calculated.	Density at $t°$ calculated.	μ_D at $t°$.	Mol. refraction at $t°$. Found.	Calculated.
Tributyrin	Below − 70°	1·0324	1·0143	0·9963		20°	292·67	294·34	1·0265	1·43587	76·50	75·98
Tricaproin ■	Between − 60° and − 25°	0·9817	0·9651	0·9494		20	393·43	394·39	0·9793	1·44265	104·24	103·64
Tricaprylin ■	8—8·3	0·9540	0·9382	0·9231		20	492·97	493·96	0·9521	1·44817	132·01	131·63
Tricaprin *	31·1		0·9205	0·9057		40	602·26	602·29	0·9205	1·44461	160·17	159·56
Trilaurin	46·4			0·8944		60	713·82	714·40	0·8937	1·44039	188·27	187·68
Trimyristin	56·6			0·8848		60	816·58	817·06	0·8843	1·44285	216·44	215·73
Tripalmitin ■	65·1				0·8657	80	931·72	933·49	0·8641	1·43807	244·62	243·99
Tristearin	71·6				0·8621	80	1033·12	1036·57	0·8592	1·43987	272·21	272·13

stream of dry air being kept passing through the mixture in order to remove the water formed, and thus prevent a limit of etherification being reached. By this device, the use of dehydrating agents, which possibly might cause secondary changes, was rendered unnecessary. The glycerol and fatty acids employed were, in all cases, carefully purified; the tables on p. 668 give the physical properties of the substances dealt with. The salts marked with an asterisk in Table II have not been hitherto prepared; the "calculated" values, in the same table, of the molecular refractions and molecular volumes were obtained from the mean values of the same constants for glycerol, water, and the corresponding acid, at the same temperature, as given in Table I. From his values for the melting point of the fatty acids and their glycerides, the author concludes that Berthelot's statement that the normal glyceric salts always melt at a lower temperature than the corresponding acids is not justified. In both tables, the molecular refraction is calculated by the Lorentz-Lorenz formula. W. A. D.

Formation of Chains. Ethylic Salts of α-Bromo-Fatty Acids with (**XXXVI**) Sodium Methoxide, (**XXXVII**) Sodium Ethoxide, and (**XXXVIII**) Sodium Propoxide and Isopropoxide. By CARL A. BISCHOFF (*Ber.*, 1899, **32**, 1748—1755; 1755—1761; 1761—1766. Compare this vol., i, 202, &c.).—The ethylic salt (1 or 2 mols.) was added to the alkyloxide (1 mol.) suspended in light petroleum, and the whole boiled until it became neutral in reaction, for which purpose 20—90 minutes usually sufficed, although in the case of the ethoxide and isovalerate 160 minutes were necessary. (The alkyloxide was usually prepared by evaporating a solution of sodium in the alcohol at 170° under diminished pressure; under these circumstances, however, sodium isopropoxide is largely decomposed into sodium hydroxide and propylene, and so it was prepared by boiling sodium with light petroleum and the calculated amount of the alcohol until all the sodium had disappeared.) The possible products, taking the case of ethylic bromisobutyrate, $CMe_2Br\cdot COOEt$, and sodium methoxide as an example, are ethylic methoxyisobutyrate, $OMe\cdot CMe_2\cdot COOEt$; the sodium salts resulting from the hydrolysis of this and the original ethereal salt, $OMe\cdot CMe_2\cdot COONa$ and $CMe_2Br\cdot COONa$; unsaturated ethylic methacrylate, $CH_2\!:\!CMe\cdot COOEt$, and its polymeride, $COOEt\cdot CMe\!<\!{{CH_2}\atop{CH_2}}\!>\!CMe\cdot COOEt$, and also the sodium salts corresponding with these. The sodium salts and sodium bromide were filtered off, washed with ether, and weighed; the weight of sodium bromide was determined by titration with silver, and that of the sodium salts resulting from hydrolysis by difference. The filtrate was freed from light petroleum and ether, weighed in the crude state, and distilled fractionally, attention being paid to the size of the fractions, which were collected during equal intervals of temperature. Alkyloxy-salts and the corresponding unchanged bromo-salts come over at about the same temperature, the unsaturated salts at a lower temperature, and the polymerides at a higher temperature. The ethereal salts experimented with were those of α-bromopropionic, α-bromobutyric,

α-bromisobutyric, and α-bromisovaleric acids, and, in one case, of bromacètic acid also. In nearly all cases, only alkyloxy-salt and unchanged bromo-salt were obtained; the exceptions were those of sodium propoxide with the isobutyrate and isovalerate, when a considerable amount of the unsaturated salt, or of its polymeride, was obtained. The reaction was more rapid with methoxide than with ethoxide; still more so with propoxide; less rapid again with isopropoxide. Of the methoxide, ethoxide, propoxide, and isopropoxide respectively, about 85—95, 73—92, 70—72, and 67—76 per cent. reacted with the bromine of the bromo-salt, the rest acting as a hydrolysing agent; the first amount is fairly constant for the different ethereal salts, except that it is usually lower in the case of the isovalerate. Some experiments were made with sodium ethoxide when this was employed in alcoholic solution instead of suspended in light petroleum; in these, relatively more sodium (94—95 per cent.) reacted with the bromine, and in the case of the isovalerate, unsaturated salt was obtained as well as ethoxy-salt, and the more the higher the temperature at which the reaction was effected.   C. F. B.

Formation of Chains. Ethylic Salts of α-Bromo-Fatty Acids with (XXXIX) Sodium Butoxides, (XL) Sodium Isoamyloxide, Octyloxide and Isocapryloxide, and (XLI) Sodium Derivatives of Saturated Monhydric Alcohols. By CARL A. BISCHOFF (*Ber.*, 1899, 32, 1940—1947; 1948—1953, and 1953—1960. Compare preceding abstract).—The author has quantitatively studied the action of ethylic α-bromopropionate, α-bromobutyrate, α-bromisobutyrate, and α-bromisovalerate on the sodium derivatives of methylic, ethylic, propylic, butylic, octylic, isopropylic, secondary butylic, isocaprylic, $CH_2Me \cdot [CH_2]_3 \cdot CHMeOH$, isobutylic, isoamylic, $CHMe_2 \cdot CH_2 \cdot CH_2OH$, and tertiary butylic alcohols. After boiling equivalent quantities of the bromo-ester and of the sodium alkyloxide for 1 hour in light petroleum (b. p. 65—70°), the sodium was distributed as sodium bromide, sodium alkyloxide, sodium salt of the fatty acid, sodium salt of the alkyloxy-acid, or of an unsaturated acid, and each of these was separately determined.

Of the normal alcohols employed, the one with the highest molecular weight, namely, octylic, showed the least condensation with the α-bromisobutyrate and α-bromisovalerate. Of the alcohols with single side chains, isopropylic appears to be the least, and isoamylic the most, favourable for the condensation (compare Abstr., 1896, i, 467). The sodium derivative of trimethylcarbinol also gave relatively small amounts of condensation product, especially with ethylic α-bromopropionate and ethylic α-bromisobutyrate; with the normal butyrate and isovalerate, it appeared to condense more readily than did sodium isopropoxide. Somewhat remarkable is the fact that sodium isopropoxide, when heated, is decomposed into propylene and sodium oxide, whilst sodium tertiary butoxide under similar conditions is stable.

The constitution of the different alcohols does not appear to affect the condensations mentioned above to nearly the same extent as does the constitution of sodium ethylic malonates, or of aromatic bases previously studied.
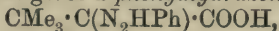
In order to determine whether the increase or contraction of volume on mixing the constituents is an important factor in the condensation, the specific increase or decrease in volume, when the alcohols are mixed with the above-mentioned ethylic salts, was determined. The greatest contractions are given with methylic alcohol, and from propylic alcohol onwards an increase in volume occurs; this increase augmenting in the following order: propylic, butylic, isobutylic, isoamylic, isopropylic, tertiary butylic, octylic, heptylic, iso-octylic. Of the four ethylic salts employed, the bromobutyrate gives a greater contraction or smaller increase than the bromopropionate, the isobutyrate a smaller contraction or larger increase than the normal butyrate, and the isovalerate a larger contraction or smaller increase than the isobutyrate.

J. J. S.

Derivatives of Pinacolin. By E. CARLINFANTI (*Gazzetta*, 1899, **29**, i, 269—275. Compare Abstr., 1898, i, 234).—*Ethylic trimethyl-pyruvate*, $CMe_3 \cdot CO \cdot COOEt$, a limpid liquid with a pungent, aromatic odour, distils at 67—68° under 15 mm. pressure, and at 0° has a sp. gr. 0·9716 at 0°/0°, and 0·9583 at 15°/15°. The *phenylhydrazone*, $CMe_3 \cdot C(N_2HPh) \cdot COOEt$, melts at 42—43°, and crystallises from dilute alcohol in beautiful, white, pearly needles which assume a yellowish tint on exposure to light. By adding the theoretical quantity of concentrated hydrochloric acid drop by drop to a mixture of molecular proportions of the ethylic salt and potassium cyanide kept at 0°, the corresponding *cyanhydrin*, $CMe_3 \cdot C(CN)(OH) \cdot COOEt$, is obtained as a limpid liquid with a faintly nitrilic aromatic odour; it boils at 119—121° under 15 mm. pressure, and has a sp. gr. 1·0462 at 0°/0°. When boiled with a slight excess of 10 per cent. aqueous potash, this cyanhydrin yields the original trimethylpyruvic acid.

Trimethylpyruvic acid gives a *phenylhydrazone*,
$$CMe_3 \cdot C(N_2HPh) \cdot COOH,$$
melting at 156—158°.

T. H. P.

Complex Platinum Salts: Oxalates and Nitrites. By MAURICE VÈZES (*Bull. Soc. Chim.*, 1899, [iii], **21**, 143—148. Compare this vol., i, 572). When oxalic acid is added to a hot, concentrated solution of potassium platosonitrite, nitrous fumes are evolved, and the liquid, on cooling, deposits yellow, optically active crystals of *potassium platoso-oxalonitrite*, $PtC_2O_4(NO_2)_2K_2 + H_2O$. If a large excess of oxalic acid is used, Söderbaum's platoso-oxalate is formed, and it appears that there is only one salt, the platoso-oxalonitrite, intermediate in composition between the platosonitrite and the platoso-oxalate. The same intermediate salt is produced by the action of potassium nitrite on either modification of potassium platoso-oxalate, by mixing solutions of molecular proportions of potassium platosonitrite and platoso-oxalate, and by the action of normal potassium oxalate on potassium platosodichloronitrite. The converse transformation of the platoso-oxalonitrite into the platoso-dichloronitrite is easily affected by adding calcium chloride to the solution of the former salt. Similar reactions are found to occur with potassium platosodibromonitrite and platosodi-iodonitrite, the oxalic acid radicle and the halogen being mutually replaceable. N. L.

Complex Palladium Salts—Pallado-oxalates. By MAURICE VÈZES (*Bull. Soc. Chim.*, 1899, [iii], 21, 172—175. Compare this vol., i, 272 and preceding abstract, also Kane, *Phil. Trans.*, 1842, 132, 297).—*Potassium pallado-oxalate*, $K_2Pd(C_2O_4)_2 + 3H_2O$, is obtained when a concentrated solution of potassium oxalate is added to a cold saturated solution of potassium palladochloride, K_2PdCl_4; it may also be obtained by the action of potassium oxalate or of oxalic acid on potassium palladonitrite, $K_2Pd(NO_2)_4$. It is sparingly soluble in cold, readily in warm, water, and undergoes decomposition when heated at 80°, or when its solutions are boiled. J. J. S.

Determination of the Molecular Weight of Ethylic Sodiomalonate and Ethylic Sodacetoacetate. By DANIEL VORLÄNDER and RUDOLF VON SCHILLING (*Ber.*, 1899, 32, 1876—1877).—Determinations of the molecular weight by the boiling point method indicate that neither ethylic sodiomalonate nor ethylic sodacetoacetate undergo dissociation in alcoholic solution into sodium ethoxide and the corresponding ethereal salt; Nef's assumption to the contrary (*Annalen*, 1897, 298, 262) is therefore not justified. The disodium derivatives of ethylic malonate and ethylic acetoacetate do not, however, exist in alcoholic solution. W. A. D.

Formation of Adipic Acid from the Fraction of Russian Petroleum which Boils at 80° and consists of Naphthenes. By OSSIAN ASCHAN (*Ber.*, 1899, 32, 1769—1772).—Markownikoff's results (this vol., i, 24) have been confirmed, and his method improved. Some of the lower boiling portion of Baku petroleum, which had not been treated with acid or alkali, was repeatedly fractionated with a fractionating column; from 20 litres of it, about 1·5 litres boiling at 78—82° and with a sp. gr. 0·752 was obtained. This is heated with ten times its weight of nitric acid of sp. gr. 1·42 in a retort with reflux apparatus for 50—60 hours, until the gas that comes off is lighter in colour; the liquid is then evaporated to dryness, the residue digested for 12 hours with an equal volume of cold water, drained and dissolved in 25 per cent. ammonia; the solution is extracted twice with ether, heated to boiling, and acidified with strong hydrochloric acid; the adipic acid which crystallises on cooling is recrystallised from a little boiling water. From 250 grams of the hydrocarbon, 44 grams of the acid were obtained, so that the method is the cheapest and most convenient one for the preparation of adipic acid.

C. F. B.

Compounds of Certain Organic Acids with Sulphuric Acid. By SEBASTIAAN HOOGEWERFF and WILLEM A. VAN DORP (*Rec. Trav. Chim.*, 1899, 18, 211—214).—On dissolving certain organic acids in concentrated sulphuric acid, well-defined, crystalline additive compounds separate, which, when exposed to the air, rapidly absorb water and are decomposed. Succinic acid, mesaconic acid, and benzoic acid yield *compounds* containing 1 mol. of sulphuric acid; the *compound* obtained from fumaric acid has the composition $C_4H_4O_4 + 2H_2SO_4$, and forms beautiful, transparent plates, whilst cinnamic acid yields two *derivatives*, having the formulæ $2C_9H_8O_2 + 3H_2SO_4$ and $C_9H_8O_2 + H_2SO_4$ respectively. W. A. D.

Action of Ethylic Sodiomalonate on the Dibromides, $C_nH_{2n}Br_2$. By WLADIMIR IPATIEFF (*J. pr. Chem.*, 1899, [ii], 59, 542—556. Compare this vol., i, 481).—By the action of sodium on ethylic malonate and β-diethyltrimethylenic bromide, there is formed a mixture of ethylic ethanetetracarboxylate and *ethylic diethylallylmalonate*, $CEt_2:CH \cdot CH_2 \cdot CH(COOEt)_2$; this is an oil boiling at 161—162° under 23 mm. pressure, and of sp. gr. 1·0017 at 0°/0°. The *acid* is an unstable oil, which yields *calcium*, *silver*, and *lead* salts, which are insoluble in water.

Ethylic methylethylallylmalonate, $CMeEt:CH \cdot CH_2 \cdot CH(COOEt)_2$, prepared in similar manner, is a colourless oil boiling at 155—156° under 24 mm. pressure, and of sp. gr. 1·0037 at 0°. The *acid* is an unstable oil, giving insoluble *calcium*, *silver*, and *lead* salts.   R. H. P.

Tautomerism. By LUDWIG KNORR (*Annalen*, 1899, 306, 332—393. Compare Abstr., 1897, i, 63; 1898, i, 65; and this vol., i, 194).—This paper contains a detailed account of the five isomeric ethylic diacetylsuccinates, a summarised description of which has already appeared.

The author has previously defined a tautomeric compound as a mixture of isomeric substances existing above the stability limit of any single component (Abstr., 1897, i, 66), but he now regards this definition as being too general, and therefore arranges tautomeric substances in two classes; those composed of isomerides capable of mutual interconversion are called *allelotropic* mixtures, pseudomeric compounds being those mixtures in which the conversion can proceed in only one direction. The ethylic diacetylsuccinates and ethylic dibenzoylsuccinates may be regarded as instances of allelotropism, along with the dibenzoylacetylmethanes (Claisen, Abstr., 1896, i, 557), the ethylic mesityloxidoxalates (*loc. cit.*), the tribenzoylmethanes (*loc. cit.*), and the parabromobenzoyldibenzoylmethanes; cases of pseudomerism are to be found in benzoyldiacetylmethane, parabromobenzoylacetone, isocarbopyrotritaric acid (this vol., i, 194), and isophenylnitromethane (Hantzsch and Schultze, Abstr., 1896, i, 672).

Solutions of the five isomeric ethylic diacetylsuccinates yield, more rapidly when heated, identical allelotropic mixtures, in which the proportion of enolic to ketonic form depends on the nature of the solvent; this proportion is approximately 1:1 in benzene and chloroform, and 3:7 in ether and petroleum, appearing to be independent of dilution and temperature. Similar remarks apply to the fused esters at temperatures above 90° (at which the β-modification melts), the proportion of enolic to ketonic form being 3:2. The stability limits of the five isomerides appear to coincide with their melting points, and consequently the a_1-ester cannot be preserved, but slowly becomes crystalline, even when strongly cooled; the spontaneous conversion of the solid a_2- and γ-modifications into the β-ester is probably due to associated traces of solvent, acting as a catalytic agent. The frequency with which the β-ester is encountered depends on its comparatively high melting point and sparing solubility, and not on relative stability. The conversion of the liquefied enolic esters into the β-ketone proceeds very slowly, but is considerably hastened by the

influence of small quantities of caustic soda, ammonia, or amines; if sodium carbonate is employed, the product contains the second inactive γ-ketone, which is obtained only by this method.

The author's experiences with the three isomeric ethylic dibenzoylsuccinates serve to develop the results obtained with the diacetylsuccinic esters. In the fused and dissolved states, they yield allelotropic mixtures consisting chiefly of the ketones, but identical mixtures are obtained from the α-, β-, and γ-modifications.

It is not possible to do justice in an abstract to the experimental work described in this paper; summaries of the results have already appeared. M. O. F.

Polyaspartic Acids. By Hugo Schiff (*Gazzetta*, 1899, 29, i, 319—340; and *Annalen*, 1899, 307, 231—246. Compare Abstr., 1898, i, 67; this vol., i, 195).—Although octaspartide unites with 8 mols. of aniline or phenylhydrazine, it only takes up 2 or 3 mols. of ammonia. Octaspartide dissolves in dilute aqueous ammonia, giving a yellow liquid, which, on evaporating, drying, and again treating with aqueous ammonia, gives a yellowish, somewhat crystalline, *ammonium octaspartate*, $C_{32}H_{34}(NH_4)_8N_8O_{25}$; it is a fairly stable salt, and cannot be converted into an amido-compound by heating.

[With Giulio Marzichi.]—When octaspartide is acted on by a current of dry ammonia, it turns reddish-yellow, *octaspartotriamide*, $C_{32}H_{26}N_8O_{17},3NH_3$ being formed. This compound loses ammonia, yielding the more stable *octaspartodiamide*, $C_{32}H_{26}N_8O_{17},2NH_3$, which is slightly soluble in water in the cold, but more so on heating, giving a neutral solution; it is insoluble in benzene, alcohol, chloroform, or carbon bisulphide. The ammonia of the stable diamide is probably combined with the end terms of the octaspartic chain. Whilst 1 molecular proportion of octaspartic acid neutralises 8 equivalents of alkali, the diamide requires in the cold only 3, and on heating 5, equivalents of alkali for its neutralisation. If octaspartodiamide is dissolved in a small quantity of normal potash solution and the liquid just acidified with acetic acid, the addition of copper acetate precipitates a *copper* derivative, $C_{32}H_{38}Cu_3N_{10}O_{23}$, with from 16 to 18 H_2O. On decomposing this copper salt with hydrogen sulphide, *diamidooctaspartic acid*, $C_{32}H_{44}N_{10}O_{23}$, is obtained; it forms a yellowish, glossy, hygroscopic mass having a strong acid reaction, and readily gives the biuret reaction with potash and copper sulphate.

[With Vieri Sevieri.]—The removal of the amido-groups from the polyaspartic acids only takes place with great difficulty. When a slight excess of sodium nitrite is gradually added to a cold aqueous solution of octaspartic acid, two of the amido-groups are transformed into hydroxyl groups, giving rise to the nonobasic *dimalohexaspartic acid*, $C_{32}H_{26}(NH_2)_6(OH)_2O_{25}$, which forms a hygroscopic, glassy mass. It gives two greenish-blue basic *copper* salts, $C_{32}H_{31}Cu_3(CuOH)_3N_6O_{27}$ and $C_{32}H_{31}Cu_2(CuOH)_5N_6O_{27}$, and a *lead* salt, $C_{32}H_{31}Pb_4(PbOH)N_6O_{27}$.

Tetraspartic acid, like the octo-compound, gives up two amidogroups, which, however, are more readily removed. In both cases, the two malic groups produced are at the ends of the polyaspartic chain. Thus tetraspartic acid, on treatment with sodium nitrite,

gives rise to the pentabasic *dimalodiaspartic acid*, $C_{16}H_{20}N_2O_{15}$, which forms a normal and a basic *lead* salt of the composition $Pb(C_{16}H_{15}Pb_2N_2O_{15})_2$ and $C_{16}H_{15}Pb(PbOH)_3N_2O_{15}$ respectively, and a basic *copper* salt, $C_{16}H_{15}Cu_2(CuOH)N_2O_{15}$. T. H. P.

Chemistry of [Organic Compounds of] Mercury. By HEINRICH LEY and H. KISSEL (*Ber.*, 1899, 32, 1357—1368).—See this vol., ii, 485.

Preparation of Ketocumaran and Analogous Compounds. By PAUL FRIEDLÄNDER (*Ber.*, 1899, 32, 1867—1869. Compare Abstr., 1897, i, 424).—Ketocumaran (cumaranone), $C_6H_4\!<\!^O_{CO}\!>\!CH_2$, can be prepared by the action of dehydrating agents on phenoxyacetic acid, but the yield is very small. When sodium or sodium ethoxide acts on ethylic orthocarboxyphenoxyacetate,

$$COOEt \cdot C_6H_4 \cdot O \cdot CH_2 \cdot COOEt,$$

however, *ethylic ketocumarancarboxylate*, $C_6H_4\!<\!^O_{CO}\!>\!CH \cdot COOEt$, is produced in good yield (compare the synthesis of ethylic indoxylate, Vorländer and Schilling, Abstr., 1898, i, 682); it melts at 65°, dissolves readily in the ordinary solvents, crystallises from dilute alcohol in silky flakes or needles, and can be distilled in a current of steam. The *methylic* salt melts at 105°. The *acid* is unstable, and when distilled in a current of steam, loses carbonic anhydride and is converted into ketocumaran. Other derivatives of ketocumarancarboxylic acid can be prepared in a similar manner. T. M. L.

Synthesis of some Furfuran Derivatives. By FRANZ FEIST and WILHELM MOLZ (*Ber.*, 1899, 32, 1766—1769).—When a mixture of chloracetone, $CMeO \cdot CH_2Cl$, with ethylic acetonedicarboxylate, $CO(CH_2 \cdot COOEt)_2$, is treated with ammonia gas in the cold, a product,

$$CMe\!<\!^{CH \cdot C \cdot COOEt}_{NH\ \ C \cdot CH_2 \cdot COOEt},$$
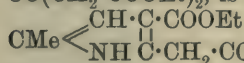
would be expected. In reality but a very little of this is formed; the main product is *ethylic 3-carboxy-2-methyl-furfuran-4-acetate*, $CH\!<\!^{CMe \cdot C \cdot COOEt}_{O——C \cdot CH_2 \cdot COOEt}$; this boils at 177—179° under 25 mm. pressure; when hydrolysed with an alkali, it yields a mixture of the corresponding dibasic acid and its ethylic hydrogen salt, of which the former is less soluble in ether. *Carboxymethylfurfuran-acetic acid* melts at 196·5°; when heated, it loses carbonic anhydride, and yields 2 : 4-dimethylfurfuran-3-carboxylic acid (Abstr., 1893, i, 403). The *ethylic hydrogen* salt, $CH\!<\!^{CMe \cdot C \cdot COOEt}_{O——C \cdot CH_2 \cdot COOH}$, melts at 109° and forms triclinic crystals [$a : b : c = 0·7112 : 1 : 0·7358$; $a = 93°\ 40'$, $\beta = 111°\ 22'$, $\gamma = 112°\ 22'$]; when heated, it loses carbonic anhydride and yields an ethylic salt from which 2 : 4-dimethylfurfuran-3-carboxylic acid is obtained on hydrolysis. C. F. B.

Ethylene-acetonitrile. By LOUIS HENRY (*Rec. Trav. Chim.*, 1899, 18, 228—232).—The substance obtained on distilling γ-chlorobutyro-nitrile with powdered caustic potash, which the author considered to

be vinylacetonitrile, $CN \cdot CH_2 \cdot CH:CH_2$ (this vol., i, 257), is in reality *ethylene-acetonitrile* [*trimethylenecarbonitrile*], $\underset{CH_2}{\overset{CH_2}{>}}CH \cdot CN$; it does not combine additively with bromine, and, when hydrolysed yields trimethylenecarboxylic acid, $\underset{CH_2}{\overset{CH_2}{>}}CH \cdot COOH$ (Perkin, Trans, 1885, 815 ; Fittig and Röder, Abstr., 1885, 653).

In conclusion, the author points out that saturated nitriles of the type $R \cdot CN$ boil at approximately the same temperature as the corresponding ethylic salts, $R \cdot COOEt$. W. A. D.

Condensation of Ethylic Oxalate with Ethereal Salts of the Glutaric Acid Series. By W. DIECKMANN (*Ber.*, 1892, **32**, 1930—1935).—*Diethylic 2-methyl-4 : 5-diketopentamethylene-1 : 3-dicarb-oxylate*, $CHMe\underset{CH(COOEt) \cdot CO}{\overset{CH(COOEt) \cdot CO}{<}}$ prepared by boiling ethylic β-methylglutarate (1 mol.) and ethylic oxalate (1 mol.) with sodium ethoxide (2 mols.), separates from alcohol in prismatic crystals and melts at 108°. Orthophenylenediamine converts it into the *phenazine* derivative which crystallises from hot alcohol in yellow needles, melts at 160—161°, dissolves in organic solvents with a greenish-blue fluorescence, and when dissolved in concentrated hydrochloric or sulphuric acid gives the bright red coloration characteristic of quinoxaline derivatives, the colour being destroyed on adding water, but not on adding acetic acid. *Diethylic 2-phenyl-4 : 5-diketopentamethylene-1 : 3-di-carboxylate*, $CHPh\underset{CH(COOEt) \cdot CO}{\overset{CH(COOEt) \cdot CO}{<}}$ is less soluble than the preceding compound, and when crystallised from absolute alcohol melts at 160—161°.

Diethylic 2 : 2-dimethyl-4 : 5-diketopentamethylene-1 : 3-dicarboxylate, $CMe_2\underset{CH(COOEt) \cdot CO}{\overset{CH(COOEt) \cdot CO}{<}}$ is formed by the action of sodium ethoxide on ethylic ββ-dimethylglutarate and ethylic oxalate, but the yield is very much smaller than in the case of the monomethyl compound, showing that the second methyl group hinders the condensation ; it melts at 96°, and closely resembles the monomethyl compound ; a better yield is obtained when the methylic salts are used and the resulting *dimethylic* salt melts at 117°, whilst its *phenazine* derivative crystallises from methylic alcohol in yellow flakes and melts at 187—188°. On reduction, this acid would yield an acid having the formula assigned by Bredt to norcamphoric acid (Marsh and Gardner's camphopyric acid), but this reduction has not yet been accomplished.

T. M. L.

Chlorination by Means of Ferric Chloride : General Method for the Preparation of Chloriodo-derivatives. By VICTOR THOMAS (*Bull. Soc. Chim.*, 1899, [iii], **21**, 286—288).—The use of ferric chloride as a chlorinating agent can be extended to the preparation of mixed haloid derivatives. Thus, on heating a mixture of ferric chloride and iodobenzene, chloriodobenzene is formed, but secondary reactions also take place, resulting in the liberation of iodine. T. H. P.

Action of Sodium Ethoxide on Tribromodinitrobenzene.
By C. LORING JACKSON and WALDEMAR KOCH (*Amer. Chem. J.*,
1899, **21**, 510—528).—The process adopted for the preparation of
symmetrical tribromodinitrobenzene $[Br_3 : (NO_2)_2 = 1 : 3 : 5 : 2 : 4]$ is
summarised, and a number of products of the action of sodium
ethoxide on it are described, in addition to the dinitroresorcinol diethylic
ether melting at 133° (Abstr., 1891, 1025), which is now shown to
have the structure $[(OEt)_2 : (NO_2)_2 = 1 : 3 : 6 : 4]$.

Tribromodinitrobenzene was dissolved in benzene and heated at 70°
for 10 minutes with an alcoholic solution of sodium ethoxide (3 mols.);
from the portion soluble in water, no definite product could be isolated,
but by extracting the portion insoluble in water with light petroleum,
a *bromodinitroresorcinol diethylic ether* was isolated melting at 92°
and isomeric with the compound melting at 184°, which forms the
chief product when the action takes place in the cold; as the con-
stitution of the latter is proved below, the former compound must
have the structure $[(OEt)_2 : (NO_2)_2 : Br = 1 : 3 : 2 : 4 : 5]$; it crystallises
in bunches of white needles, dissolves readily in cold benzene, ether,
chloroform, acetone, acetic acid, carbon bisulphide, ethylic acetate,
boiling alcohol, or light petroleum, but is insoluble in water; it
becomes brown by long exposure to air, especially in bright light;
boiling caustic soda has little or no action on it, but heating with
sodium ethoxide converts it almost quantitatively into dinitrophloro-
glucinol triethylic ether. A small quantity of a *substance* melting at
112° was isolated from the mother liquors; this crystallises from
alcohol in white needles and contains bromine, but is not identical
with Benedikt's tribromoresorcinol melting at 110°. The portion
insoluble in light petroleum consists essentially of the dinitroresorcinol
diethylic ether melting at 133°, previously described (*loc. cit.*); when
boiled with sulphuric acid of sp. gr. 1·44, it is converted al-
most quantitatively into symmetrical dinitroresorcinol $[(OH)_2(NO_2)_2 =
1 : 3 : 6 : 4]$, which proves its constitution; the dimethylic ether melting
at 167° must therefore have a similar structure and not that assigned
to it by Beilstein; also the isomeric dimethylic ether melting at 67°
can no longer be regarded as having the symmetrical structure
assigned to it by Beilstein, since this belongs to the ether melting at
167°. A small quantity of the bromodinitroresorcinol diethylic ether
melting at 184° was isolated from the mother liquors, showing that
the heating was not sufficiently prolonged to convert it completely
into dinitroresorcinol diethylic ether. The chief products of the action
are therefore dinitroresorcinol diethylic ether (16 per cent.) and
bromodinitroresorcinol diethylic ether melting at 92° (9 per cent.),
whilst 75 per cent. of the substance was converted into tarry matter.

When a mixture similar to that used in the previous experiment
was allowed to act for three to five days in the cold, a somewhat
different series of products was obtained. The aqueous liquors yielded
a considerable quantity (6 per cent. of the quantity of tribromodinitro-
benzene taken) of a dinitroresorcinol ethylic ether $[OH : OEt : 2NO_2 =
1 : 3 : 6 : 4]$ melting at 77°, and possibly identical with the compound
melting at 75° described by Arönheim (Abstr., 1879, 465), and also
gave about 1 per cent. of tribromonitrophenol $[OH : NO_2 : 3Br =$

1 : 3 : 2 : 4 : 6] melting at 90°. The portion insoluble in water was extracted with light petroleum, which deposited crystals of dinitrophloroglucinol triethylic ether melting at 105°; this does not dissolve at all in light petroleum when pure, but a yield of about 19 per cent. of the original substance was obtained from the extract. The mother liquor yielded about 19 per cent. of the bromodinitroresorcinol diethylic ether melting at 92°, which forms the chief product when the action takes place at 70°. The residue insoluble in light petroleum gave a 22 per cent. yield of the bromodinitroresorcinol diethylic ether melting at 184°, and as this is converted by the further action of sodium ethoxide into the dinitroresorcinol diethylic ether melting at 133°, it must have the constitution $[(OEt)_2 : (NO_2)_2 : Br = 1 : 3 : 6 : 4 : 5]$; in this case, therefore, the rule holds good that the replacement of a halogen atom by hydrogen only takes place when it is adjacent to two nitro-groups; in the isomeric compound in which the bromine atom is adjacent to only one nitro-group, it is displaced by an ethoxy-group as described above. About 33 per cent. of the original substance remains unaccounted for, and represents the loss incurred in purifying the various products by repeated crystallisation.

The paper also contains a discussion of the 'loosening' influence of the various radicles on one another which renders possible their displacement by the action of sodium ethoxide.   T. M. L.

Action of Acid Solutions of the Lead Salts of Monobasic Fatty Acids on Monochloro- or Monobromo-aromatic Hydrocarbons in which the Halogen is in the Side Chain. By F. BODROUX (*Bull. Soc. Chim.*, 1899, [iii], **21**, 288—291).—The preparation of aromatic ethereal salts, usually carried out by the action of an alcoholic solution of the sodium salt of the acid on halogenated aromatic hydrocarbons having the halogen in the side-chain, is considerably facilitated by using, in place of the sodium salt, the lead salt dissolved in the corresponding acid.

Thus on heating benzylic chloride with an acetic acid solution of lead acetate, lead chloride is precipitated and about 60 per cent. of the theoretical yield of pure benzylic acetate is obtained. Similarly, from lead isobutyrate and benzylic chloride, benzylic isobutyrate is formed and parabromobenzylic bromide and lead acetate yield parabromobenzylic acetate; as the latter is hydrolysed by alcoholic potash, the method gives a ready means of obtaining parabromobenzylic alcohol. Monobromodiphenylmethane and lead acetate react with the production of diphenylmethylic acetate, from which, on hydrolysis, diphenylcarbinol is easily obtained. When monobromotriphenylmethane and lead acetate are heated together, triphenylcarbinol is obtained, the triphenylmethylic acetate suffering decomposition.   T. H. P.

Action of Lead Acetate in Acetic Acid Solution on Benzylidenic Chloride and on Benzotrichloride. By F. BODROUX (*Bull. Soc. Chim.*, 1899, [iii], **21**, 331—333).—The action of lead acetate in acetic acid solution on benzylidenic chloride at the boiling temperature affords a rapid and economical method for preparing benzylidenic acetate. When, however, benzotrichloride is similarly treated, it is

wholly converted into benzoic acid, although it is probable that the triacetate, $CPh(OAc)_3$, is first produced. **N. L.**

Glyoxaldicatechol [Dicatechol Acetylenic Ether]. By CHARLES MOUREU (*Bull. Soc. Chim.*, 1899, [iii], **21**, 101—105).—*Glyoxaldicatechol* [*dicatechol acetylenic ether*], $C_6H_4{<}^O_O{>}CH \cdot CH{<}^O_O{>}C_6H_4$, formed by the action of acetylenic tetrabromide (1 mol.) on catechol (2 mols.) in the presence of aqueous potash at 60°, crystallises from alcohol in thin scales melting at 88—89°, and is converted by heating with dilute sulphuric acid into catechol (1 mol.) and a *substance* of the composition $C_8H_8O_4$, which crystallises in white, nacreous scales melting at 130—131°, is more or less soluble in water and the usual organic solvents, gives an intense blue coloration with ferric chloride, slowly reduces ammoniacal silver nitrate solution in the cold, and forms a *phenylhydrazone* which crystallises in rectangular, white scales melting and decomposing at 193°. It exhibits the characters of a monobasic acid, yields an anhydride crystallising in elongated prisms melting at 54—56°, and was proved to be identical with Majert's orthohydroxyphenoxyacetic acid, $OH \cdot C_6H_4 \cdot O \cdot CH_2 \cdot COOH$, obtained by the action of chloracetic acid on catechol (Ger. Pat. 87336 and 87669, 1895). In the formation of this acid by the hydrolysis of dicatechol acetylenic ether, it is suggested that compounds of the composition $C_6H_4{<}^O_O{>}CH \cdot CHO$ and $OH \cdot C_6H_4 \cdot O \cdot CH(OH) \cdot CHO$ are intermediate products. **N. L.**

Conversion of Hydroresorcinol into Glutaric Acid. By DANIEL VORLÄNDER and M. KOHLMANN (*Ber.*, 1899, **32**, 1878—1879). —Merling has stated (Abstr., 1894, i, 177) that when hydroresorcinol is oxidised with potassium permanganate, glutaric and succinic acids are formed; it is now shown that the oxidation is more easily carried out by using a 10 per cent. solution of an alkaline hypobromite, when glutaric acid is the sole product. Dimethylhydroresorcinol under these conditions gives rise to $\beta\beta$-dimethylglutaric acid (compare Komppa, this vol., i, 573), whilst methyl-, phenyl- and furyl-hydroresorcinol yield respectively the corresponding β-glutaric acids. In all cases, small quantities of bromohydroresorcinol are formed during the oxidation; when alkaline hypochlorites are employed, chlorohydroresorcinols are the principal products, little oxidation taking place. **W. A. D.**

Action of Chlorine on Homologues of Phloroglucinol. By MAX SCHNEIDER (*Monatsh.*, 1899, **20**, 401—423).—*Pentachlorotriketomethyl-R-hexylene*, $CO{<}^{CMeCl \cdot CO}_{CCl_2 \text{---} CO}{>}CCl_2$, prepared by the action of dry chlorine on dry methylphloroglucinol suspended in carbon tetrachloride, crystallises in lustrous plates, melts at 50°, and is very easily soluble in anhydrous ether, benzene, light petroleum, or carbon tetrachloride. *Dichloromethylphloroglucinol*, $OH \cdot C{<}^{CMe \cdot C(OH)}_{CCl=C(OH)}{>}CCl$, obtained by reducing the triketone with stannous chloride or potassium iodide, crystallises from ethylic acetate in small, colourless, lustrous

needles which rapidly become pink on exposure to moist air, melts at 112—113°, is very sparingly soluble in water but easily in ethylic acetate, benzene, or alcohol, and crystallises with $3H_2O$. The *triacetyl* derivative crystallises from alcohol or acetic acid in colourless leaflets, melts at 166°, is insoluble in water, easily soluble in warm alcohol, and sparingly so in ether or benzene. By the action of water on pentachlorotriketomethyl-*R*-hexylene, *dichloromethyl α-chlorethyl ketone* is formed together with dichloracetic acid ; it is a colourless liquid, boils at 72—74° under 25—26 mm. pressure, is insoluble in water, but easily soluble in ether, benzene, or light petroleum, and when reduced with sodium amalgam yields a liquid with a sweet alcoholic odour.

By the action of chlorine on moist methylphloroglucinol suspended in carbon tetrachloride, a compound, $C_5H_3Cl_3O_2$, which is probably a tetramethylene derivative, $CCl_2{<}^{CO}_{CO}{>}CMeCl$, is obtained ; it crystallises from benzene in colourless, lustrous needles, melts at 216°, is insoluble in water, and is decomposed by dilute potassium hydroxide solution.

Tetrachlorotriketodimethyl-R-hexylene, $CO{<}^{CMeCl\cdot CO}_{CMeCl\cdot CO}{>}CCl_2$, prepared by the action of dry chlorine on dimethylphloroglucinol, crystallises from light petroleum in large, colourless plates, has a camphorlike odour, melts at 44°, boils at 149—150° under 28 mm. pressure, is insoluble in water, easily soluble in light petroleum or benzene, soluble in ethylic acetate or ether, and dissolves in alcohol with partial decomposition. When reduced with stannous chloride, it forms *monochlorodimethylphloroglucinol,* $OH\cdot C{<}^{CMe\cdot C(OH)}_{CMe:C(OH)}{>}CCl$, which crystallises from chloroform in small, matted needles, is odourless, melts at 160—161°, is easily soluble in the ordinary solvents, but almost insoluble in water. The *triacetyl* derivative separates from ethylic acetate or acetic acid in colourless crystals and melts at 170°. Tetrachlorotriketodimethyl-*R*-hexylene is much more slowly attacked by water than pentachlorotriketomethyl-*R*-hexylene, and at the ordinary temperature requires several days for any appreciable reaction to occur. When heated with water at 120—150°, a strongly acid product with a penetrating odour and a brown, tarry mass is obtained from which no characteristic compounds were isolated.

Trichlorotriketotrimethyl-R-hexylene, $CO{<}^{CMeCl\cdot CO}_{CMeCl\cdot CO}{>}CMeCl$, prepared by the action of dry chlorine on trimethylphloroglucinol, crystallises in colourless, transparent plates, melts at 49—50°, boils at 141° under 28 mm. pressure, is easily soluble in warm benzene, carbon tetrachloride, chloroform, ether, or light petroleum, and when reduced with stannous chloride yields trimethylphloroglucinol. Trichlorotriketotrimethyl-*R*-hexylene is only partially decomposed by water at 150°, forming tarry products with the odour of pyrotartaric acid. The triketone dissolves slowly in dilute potassium hydroxide solution, forming a brownish-yellow solution from which acids liberate carbonic anhydride and precipitate a white sub-

stance which crystallises in leaflets, melts at 142—143°, is soluble in ether, and on remaining in a vacuum over sulphuric acid decomposes into a viscous mass which is insoluble in potassium hydroxide solution. This compound has possibly a lactonic constitution. E. W. W.

Nitro-derivatives. By ANGELO ANGELI (*Gazzetta*, 1899, **29**, 275—277).—The author finds that the compound prepared by him by the action of alkali on isosafrole nitrosite (Abstr., 1896, i, 477), to which he gave the formula $CH_2:O_2:C_6H_3\cdot CH:CMe\cdot NO_2$, differs from true nitro-derivatives in not reacting with hydroxylamine. With potash, however, it forms a salt which is decomposed by acetic acid with the precipitation of the original nitro-compound. This behaviour may be explained by supposing the group $-CH:C\cdot NO_2-$ to change into the isomeric form $\begin{matrix} -C:C- \\ | \ \ | \\ O\cdot NOH \end{matrix}$. T. H. P.

Action of Sodium Phenoxide on the Dibromo-derivatives of Hydrocarbons. By WASSILY A. SOLONINA (*Chem. Centr.*, 1899, i, 248—249; from *J. Russ. Chem. Soc.*, 1898, **30**, 826—842. Compare this vol., i, 473).—(1) $\alpha\beta$-Dibromopropane, when treated with a 25 per cent. solution of sodium phenoxide in alcohol, forms mainly α-bromopropylene with some β-bromopropylene. (2) $\alpha\gamma$-Dibromopropane, under similar conditions, yields phenylic allylic ether, $PhO\cdot C_3H_5$, boiling at 188—193° and diphenoxypropane, $CH_2(CH_2\cdot OPh)_2$, which melts at 61°, whilst from (3) $\alpha\beta$-dibromisobutane, $CMe_2Br\cdot CH_2Br$, only α-bromisobutylene, $CMe_2:CHBr$, boiling at 89—92° is obtained. (4) $\beta\gamma$-Dibromobutane forms β-bromobutylene, $CMeBr:CHMe$, and a small quantity of an unsaturated substance which is volatile in steam and is probably the *compound* $OPh\cdot CMe:CHMe$. (5) By the action of sodium phenoxide on $\alpha\delta$-dibromopentane, *α-phenoxy-3-pentylene*, $CHMe:CH\cdot CH_2\cdot CH_2\cdot OPh$, and *$\alpha\delta$-diphenoxypentane* are obtained. The former is a liquid with a characteristic odour, boils at 226—227°, is volatile in steam, easily soluble in alcohol, ether or benzene, and combines readily with bromine. The latter separates in white crystals, melts at 48—49°, is slightly soluble in cold, easily in hot, alcohol, and in benzene or ether; when heated with hydrobromic acid at 160—170°, it forms the original dibromopentane. (6) $\alpha\epsilon$-Dibromohexane yields *α-phenoxy-δ-hexylene*, $CHMe:CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot OPh$, and *$\alpha\epsilon$-diphenoxyhexane*. The former is a colourless oil, boils at 243—246°, and is easily soluble in alcohol, ether, or benzene. The latter boils at 225—230° under 20—25 mm. pressure, is easily soluble in alcohol, ether, or benzene, and by the action of hydrobromic acid forms the original dibromohexane. (7) From $\beta\gamma$-dibromo-$\beta\gamma$-dimethylbutane, $CMe_2Br\cdot CMe_2Br$, tetramethylethylene, $CMe_2:CMe_2$, and unsaturated bromo-derivatives, probably containing bromohexylene, $C_6H_{11}Br$, are obtained. (8) $\beta\epsilon$-Dibromohexane yields mainly *$\beta\epsilon$-diphenoxyhexane*, with a small quantity of *β-phenoxy-δ-hexylene*, $CHMe:CH\cdot CH_2\cdot CHMe\cdot OPh$. The former crystallises in colourless, monoclinic leaflets (Popoff), melts at 86—86·5°, and when heated with hydrogen bromide forms the original dibromohexane; the latter is a colourless oil, boils at 235—237°, is volatile in steam, and readily unites with bromine. (9) $\alpha\zeta$-Dibromo-

hexane reacts quickly with sodium phenoxide, forming $a\zeta$-diphenoxy-hexane melting at 82·5°, together with some unsaturated compounds.

From these results, the following conclusions are drawn :—(1) Dibromo-derivatives in which the bromine atoms are in the primary position (CH_2Br) react with sodium phenoxide to form diphenoxy-derivatives, whilst (2) derivatives containing the bromine atoms united to contiguous carbon atoms in two secondary groups (CHBr), or in a primary and a secondary or in a primary and a tertiary group (CBr), yield only unsaturated bromides. (3) When the bromine atoms are contained in secondary groups separated by several carbon atoms, a mixture of saturated diphenoxy- and unsaturated mono-phenoxy-derivatives is formed. (4) When both bromine atoms are contained in tertiary groups, only unsaturated hydrocarbons are obtained.

By the action of sulphurous anhydride on the unsaturated monophenylic ethers dissolved in water or in benzene, white, amorphous compounds containing sulphur are formed ; these compounds are soluble in alkalis and are decomposed by heat. Thus ethylic allylic ether yields the *compound* $C_5H_{10}O + SO_2$, methylic allylic ether the *compound* $C_4H_8O + SO_2$, and allylic alcohol the *compound* $C_3H_6O + SO_2$. The constitution of these compounds is probably $O{<}^{CH_2}_{SO}{>}CH \cdot CH_2 \cdot OR$, for in the absence of negative groups such as COOH, COOR, halogens, &c., only substances which contain the group $CH_2{:}CH \cdot CH_2$ are capable of forming such additive products.

E. W. W.

Dimethylaniline Oxide. By EUGEN BAMBERGER and FRED. TSCHIRNER (*Ber.*, 1899, **32**, 1882—1903. Compare this vol., i, 347).— When sulphurous anhydride is passed into a dilute aqueous solution of dimethylaniline oxide at 0°, rapid action occurs and a mixture consisting of dimethylaniline (22 per cent.) and its ortho- and para-sulphonic acids (60 and 20 per cent. respectively) is obtained, together with traces of dimethylorthamidophenol and its sulphonic acid ; it is probable that the *additive* compound, $SO_3H \cdot NPhMe_2 \cdot OH$, is first formed, and that subsequent intramolecular rearrangement occurs (compare Abstr., 1897, 286, and 1898, i, 31). The fact that the orthosulphonic acid is obtained as the principal product of this change is of importance, since the direct action of sulphuric acid on dimethylaniline yields the para- and meta-acids exclusively (Evans, Proc., 1896, 234). The formation of dimethylorthamidophenol appears to be due to isomeric change in a portion of the unaltered dimethylaniline oxide, induced by the presence of sulphurous anhydride ; it is noteworthy that sulphuric acid is unable to effect this change.

On adding a solution of sodium nitrite (1 mol.) to a solution of dimethylaniline oxide in dilute hydrochloric acid at 0°, a mixture of nearly equal proportions of ortho- and para-nitrodimethylaniline is obtained, together with traces of paranitrosodimethylaniline and tetramethylbenzidine. It is probable that in this action the *nitramine* $OH \cdot NPhMe_2 \cdot NO_2$, is initially formed, but this could not be isolated owing to its readily undergoing change into the isomeric nitrodimethyl-

anilines (compare Abstr., 1894, i, 238). Orthonitrodimethylaniline (compare Friedländer, this vol., i, 350) is a mobile, orange-yellow oil which boils at 151—153° under 30—33 mm. pressure, solidifies at −20° to yellowish-red needles, is easily soluble in all organic solvents, and is volatile with steam; the *hydrochloride*, $C_8H_{10}N_2O_2,HCl$, forms snow-white, vitreous needles, and dissociates at 173—174°.

When methylic iodide is left in contact with dimethylaniline oxide dissolved in alcohol, formaldehyde is evolved and a mixture of dimethyl-aniline, its hydriodide, trimethylphenylammonium iodide and *dimethylaniline oxide sesqui-iodide*, $(NPhMe_2O)_2I_3$, obtained; the latter is more readily prepared by adding iodine dissolved in ether to a solution of dimethylaniline oxide in absolute alcohol, and forms reddish-black prisms of a steel-blue lustre which melt and decompose at a temperature between 99° and 101·5°, depending on the rate of heating; the sesqui-iodide is decomposed on keeping, and when dissolved in caustic soda, gives rise to dimethylaniline oxide. It is probable that the first product of the action of methylic iodide on dimethylaniline oxide is the *compound* $OMe·NPhMe_2I$, and that this gives rise to formaldehyde and dimethylaniline hydriodide; the latter is then decomposed by some unchanged dimethylaniline oxide, producing free iodine, which unites with the oxide of the base to form the sesqui-iodide above described.

When aqueous formaldehyde is mixed with a solution of dimethyl-aniline oxide hydrochloride acidified with dilute sulphuric acid, a solution is obtained which is coloured deep violet-blue on neutralising a portion with soda and adding a mixture of copper and sodium acetate; it is probable that this colour reaction indicates that the *additive* compound, $OH·NPhMe_2·CHO$, is formed initially, but is afterwards de-composed into formic acid and dimethylaniline, along with a small quantity of dimethylorthamidophenol.

Whereas dimethylaniline is characterised by the great activity of the hydrogen atom in the para-position to the $·NMe_2$ group, especially as regards its power of yielding condensation products, the same atom in dimethylaniline oxide appears to be quite inert; thus, the oxide does not yield azo-compounds by combining with diazo-salts, nor com-bine with formaldehyde to form an analogue of tetramethyldiamido-diphenylmethane; neither does it seem capable of forming dyes of the indamine or malachite-green type. W. A. D.

Orthamidodimethylaniline. By EUGEN BAMBERGER and FRED. TSCHIRNER (*Ber.*, 1899, **32**, 1903—1907).—*Orthamidodimethylaniline*, $C_8H_{12}N_2$, prepared by reducing orthonitrodimethylaniline (preceding abstract) with zinc dust and aqueous ammonium chloride, is a colourless, mobile oil which has a pleasant odour and boils at 99·5—101° under 20—25 mm. pressure; on adding ferric chloride to the base suspended in water, a yellowish-brown coloration is produced, which rapidly becomes violet and then blue, and finally, after a long time, deep red; a red coloration is produced immediately on adding ferric chloride to an alcoholic solution of the base. The *benzoyl* derivative, $NMe_2·C_6H_4·NHBz$, crystallises from dilute methylic alcohol in lustrous needles and melts at 51°.

When orthamidodimethylaniline is diazotised and the solution boiled, formaldehyde is evolved and methylaniline formed ; it is suggested that the compound OMe·NPhMe is possibly an intermediate product of the action. Traces only of the normal decomposition product, dimethylorthamidophenol, are obtained. W. A. D.

Preparation of a-Dinitrodimethylaniline. By JOHANNES PINNOW (*Ber.*, 1899, **32**, 1666—1669).—Orthonitrodimethylaniline (which is formed as a bye-product in the preparation of a-dinitrodimethylaniline) yields a *picrate* which crystallises in slender, yellow prisms and needles, melts at 102—103·5°, and dissolves sparingly in acetone and readily in alcohol or ether. *Orthamidodimethylaniline* is a colourless oil with an odour similar to that of menthol, and boils at 217·5° under 751·5 mm. pressure ; it solidifies, when cooled with liquid air, to a glassy mass which melts below −50° ; the alcoholic solution gives a cherry-red coloration with ferric chloride. The *hydrochloride* dissolves readily in cold water, moderately in hot alcohol, but only slightly in the cold ; on adding alcohol to a hot saturated aqueous solution, it separates in white prisms, which soon redden, and melts and decomposes at 184—186°. The *picrate* crystallises from alcohol in large, yellow, rhomboidal tablets, and melts at 138—140°. The *acetyl* derivative crystallises from light petroleum in slender, white needles and melts at 72—73° ; by the further action of acetic anhydride at 160°, it yields 1′ : 2′-dimethylbenzimidazole. T. M. L.

Derivatives of Aromatic Metadiamines. By GEORGE F. JAUBERT (*Bull. Soc. Chim.*, 1899, [iii], **21**, 18—25).—This paper gives details of the preparation of derivatives of aromatic metadiamines. The following are described for the first time.

Acetyltrimethylmetaphenylenediamine hydriodide is obtained in transparent, colourless crystals on heating acetylmetamidodimethylaniline with methylic iodide and methylic alcohol.

Nitrosometachlorodimethylaniline hydrochloride, produced by treating metachlorodimethylaniline hydrochloride with sodium nitrite, crystallises from water, alcohol, or acetic acid in golden-yellow needles ; when condensed with β-naphthol, it yields a chloro-derivative of Meldola's blue. G. T. M

Tertiary Aromatic Amines. II. By CARL HAEUSSERMANN and EUGEN BAUER (*Ber.*, 1899, **32**, 1912—1915. Compare this vol., i, 204).—When paradichlorobenzene is heated with potassium and diphenylamine in an atmosphere of hydrogen for 2 hours at 240—250°, a mixture of two *tetraphenylphenylenediamines* is obtained, together with a large proportion of resin. *a-Tetraphenylphenylenediamine*, $C_{30}H_{24}N_2$, differs from its congener in being sparingly soluble in acetone, from which it crystallises in thin, colourless, lustrous plates which melt at 199—200° ; on adding a concentrated aqueous solution of sodium nitrite to its solution in glacial acetic acid, the *nitro*-derivative, $C_{30}H_{23}N_3O_2$, separates in vermilion-coloured needles, which, when pure, melt at 167—168°. *β-Tetraphenylphenylenediamine* is a white, crystalline powder which melts at 127—129°, and is extremely soluble in acetone and ether, but sparingly in ethylic and methylic alcohols ; when treated with sodium nitrite in acetic acid solution, it

yields the *mononitro*-derivative, $C_{30}H_{23}N_3O_2$, which crystallises from glacial acetic acid in brownish-yellow, lustrous prisms and melts at 185—186°.

The formation of two tetraphenylphenylenediamines from para-dichlorobenzene is probably due to the latter partially undergoing isomeric change into metadichlorobenzene under the conditions of the experiment (compare Istrati, Abstr., 1890, 882); attempts to determine their respective structures have as yet led to no issue.

Tetraphenylorthophenylenediamine, prepared from orthodichlorobenzene, separates from alcohol as a microcrystalline powder, melts at 133—134·5°, and dissolves in concentrated sulphuric acid containing a trace of nitrate or nitrite, producing a deep blue coloration.

<div align="right">W. A. D.</div>

Corrections with Regard to Diazo-compounds. By Arthur Hantzsch (*Ber.*, 1899, 32, 1717—1721).—The author claims priority for suggesting the formulæ of the diazonium salts, $R \cdot NCl \vdots N$, and of the normal and iso-diazotates, $R \cdot N \vdots N \cdot OK$. The statement that the normal diazotates are converted smoothly by the action of benzoic chloride into nitrosobenzanilide, whilst the isodiazotates give only traces of this compound, is incorrect; both compounds give a yield of 50 to 60 per cent. of the nitrosobenzanilide, leaving a residue of 36 to 37 per cent. of normal diazotate; this is explained as being due to the formation of nitrosobenzanilide from both compounds, and the subsequent decomposition of a part of it by the excess of alkali with separation of the normal diazotate. It is also an incorrect statement that the isodiazotates are reduced most readily by sodium amalgam to the hydrazine; both normal and iso-compounds are reduced equally well in presence of an excess of alkali, and the differences which are observed in dilute aqueous solution are due to the partial hydrolysis of the normal diazotates. Similarly, in presence of an excess of alkali, the normal and iso-diazotates behave in exactly the same way on oxidation to phenylnitramine. In the formation of colours from diazo-compounds, the free diazohydrate is the active agent, and the normal diazotates condense most readily by reason of the greater amount of hydrolytic dissociation; in presence of an excess of alkali, no difference is observed. In conclusion, it is stated that the normal and iso-diazotates behave as salts of two very similar acids of different strengths, in accordance with the stereoisomeric forms of the formula, $Ph \cdot N \vdots N \cdot OK$, rather than with Bamberger's formulæ, $PhN(OK) \vdots N$, and $PhN \vdots N \cdot OK$.

<div align="right">T. M. L.</div>

Antidiazohydrates and Primary Nitrosamines. By Arthur Hantzsch, M. Schümann, and A. Engler (*Ber.*, 1899, 32, 1703—1716; compare this vol., i, 400).—Two groups of substances can be clearly distinguished; (1) true diazohydrates, $R \cdot N \vdots N \cdot OH$, electrolytes of acid reaction with definite affinity constants, which combine directly with dry ammonia gas (see note, this vol., i, 401), and interact directly with phosphorus pentachloride and acetic chloride; (2) primary nitrosamines, $R \cdot NH \cdot NO$, pseudo-acids which do not conduct, have no effect on indicators, and do not show any definite affinity constant, do not combine directly with ammonia gas, and do not interact with

phosphorus pentachloride and acetic chloride at ordinary temperatures. The primary nitrosamines never yield salts of the formula R·NK·NO, but always undergo isomeric change and yield true diazotates of the formula R·N:N·OK.

Thiele's 'nitrosourethane' is a true diazohydrate, and should be called *diazourethane* or *carbethoxydiazohydrate*. Unlike phenylnitrosamine (diazobenzenehydrate), it gives off hydrogen chloride vigorously when treated in ether or benzene solution with phosphorus pentachloride or acetic chloride, even when cooled with a freezing mixture; dry ammonia precipitates the ammonium salt from a solution of the diazohydrate in benzene. Potassium diazourethane (regarded by Thiele as potassium nitrosourethane, COOEt·NK·NO) is a neutral salt and very highly dissociated in aqueous solution; at 0°, $\mu_{32} = 42\cdot4$, $\mu_{128} = 44\cdot2$, $\mu_{512} = 45\cdot4$, and $\mu_{1024} = 45\cdot6$, whence μ_{∞} is calculated to be 46 for the potassium salt, and 221 for the free acid. Taking this value of μ_{∞} for the acid, the conductivity of its aqueous solution at different concentrations gives, for the affinity constant, $k = 0\cdot00016$ at 0°, that is, free diazourethane at 0° is an acid of about one-tenth the strength of acetic acid, and at 25° would probably be of about equal strength. Lastly, diazourethane can be titrated directly with the calculated quantity of alkali, showing it to be a true acid, and not a pseudo-acid.

Silver diazourethane reacts vigorously with methylic iodide, ethylic iodide, or benzylic iodide. *Methylic diazourethane*,' COOEt·N:N·OMe, is a yellow oil of sharp odour, miscible with organic liquids, but not with water. Unlike the isomeric nitrosomethylurethane, which can be distilled in a current of steam, it is rapidly decomposed by cold water with evolution of nitrogen, and still more rapidly by acids and alkalis. It boils unchanged at 84° under 25 mm. pressure, but is very liable to explode. Zinc dust and acetic acid reduces it to hydrazine.

Thiele's nitrosoguanidine behaves much more like a true nitrosamine; it has a neutral reaction, and when decomposed by acids yields mainly nitrous acid and not nitrogen; it does not interact with phosphorus pentachloride or acetic chloride, and the silver salt is not acted on by methylic iodide.

The so-called 'diazothiazol hydrates' and 'diazouracils' are probably true nitrosamines.

Sodium paranitroantidiazobenzene has a neutral reaction, but appears to be somewhat hydrolysed in very dilute solution. Potassium parabromantidiazobenzene is difficult to obtain free from potassium hydroxide or carbonate, and therefore has an alkaline reaction, but conductivity determinations show that it is not hydrolysed to any large extent. A mixture of this potassium salt with an equivalent quantity of hydrochoric acid had a conductivity in $N/128$ solution $\mu = 73\cdot4$ ($N/128$ KCl gives $\mu = 73\cdot9$) and in $N/256$ solution $\mu = 75\cdot0$ ($N/256$ KCl gives $\mu = 75\cdot3$), showing that the liberated parabromantidiazobenzene hydrate immediately passes into a non-conducting pseudo-acid, namely, the primary nitrosamine, $C_6H_4Br\cdot NH\cdot NO$; the resulting solution was quite neutral and free from nitrous acid. Similar results were obtained with paranitrodiazobenzene hydrate (paranitrophenylnitros-

amine), but owing to its instability the measurements were not so exact. Although the phenomenon of 'gradual neutralisation' cannot be observed, both compounds show 'abnormal neutralisation phenomena' (this vol., i, 400), that is, a neutral solution of the pseudo-acid remains neutral on adding one equivalent of alkali, and, conversely, a neutral solution of a salt remains neutral on adding one equivalent of hydrochloric acid. The nature of the two nitrosamines is also shown by the fact that, unlike diazourethane hydrate, they do not interact with phosphorus pentachloride either in the solid state or in solution, and do not act on acetic chloride when dissolved in benzene or ether, although the solids bring about an evolution of hydrogen chloride; moreover, ammonia gas does not form a salt by direct combination with the solids or with their solutions in benzene, although well-defined salts are produced in dissociating solvents, but, on the other hand, β-naphthol slowly combines with them, both in ethereal and in benzene solution.

The potassium salt of diazosulphanilic acid is probably a true diazo-compound, $SO_3K \cdot C_6H_4 \cdot N\vdots N \cdot OH + H_2O$, and not a nitrosamine, since (1) it shows an acid reaction in dilute solution, (2) has very little tendency to decompose with separation of nitrous acid, and (3) exhibits an abnormal increase of conductivity in dilute solution, the increment $\Delta_{1024-64}$ being 8·1 units at 0° as compared with 4·1 for KCl and 4·6 for NaCl, indicating that it is probably comparable to the acid salt of a dibasic acid.   T. M. L.

Direct Conversion of Aniline into Phenylhydroxylamine. By EUGEN BAMBERGER and FRED. TSCHIRNER (*Ber.*, 1899, **32**, 1675—1678. Compare Caro, *Zeit. angew. Chem.*, 1898, 845).—When aniline is oxidised by a persulphate in presence of ether and in contact with ice, the amount of nitrosobenzene produced is only small, and by extracting the ethereal solution with hydrochloric acid, a solution is obtained which gives all the characteristic reactions of phenylhydroxylamine. In order to separate this from the aniline which is also present, diazobenzene chloride is added, and the phenylhydroxylamine separated in the form of phenylazohydroxyanilide, $N_2Ph \cdot NPh \cdot OH$ (Abstr., 1896, i, 222); this crystallises from light petroleum in yellow needles melting at 126—127°, and the alcoholic solution gives a deep blue coloration with a little ferric chloride, and a green coloration on the addition of more ferric chloride; it dissolves in caustic alkalis, forming a yellow salt; chromic acid oxidises it to nitrosobenzene.

Phenylazohydroxyorthotoluidide, $C_6H_4Me \cdot N(OH) \cdot N_2Ph$, prepared in a similar way from orthotoluidine, crystallises in feebly-yellow, silky needles, melts at 79—79·5°, dissolves moderately in alcohol or light petroleum when hot, but only slightly in the cold. The corresponding *para*-compound crystallises from light petroleum in lemon-yellow, silky needles and melts at 124°. Both compounds give the characteristic blue to green coloration on adding ferric chloride to an alcoholic solution.

The direct conversion of aniline into phenylhydroxylamine completes the series of oxidations from aniline to nitrobenzene, thus:
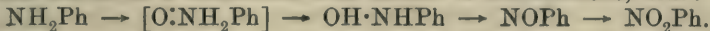
$$NH_2Ph \longrightarrow [O\vdots NH_2Ph] \longrightarrow OH \cdot NHPh \longrightarrow NOPh \longrightarrow NO_2Ph.$$
                T. M. L.

Compounds of Phenylhydrazine with Metallic Thiosulphates, Dithionates, and Hypophosphites. By JOSEPH MOITESSIER (*Bull. Soc. Chim.*, 1899, [iii], **21**, 336—338. Compare Abstr., 1898, i, 132, 133, 413; this vol., i, 205).—*Cadmium thiosulphate phenylhydrazine*, $CdS_2O_3,2N_2H_3Ph$, obtained by mixing solutions of phenylhydrazine, cadmium sulphate, and sodium thiosulphate, crystallises in slender needles which begin to decompose at about 160°, but do not melt below 250°. It is very slightly soluble in cold, more soluble in hot, water or alcohol, and insoluble in ether and chloroform, which, however, gradually decompose it. The corresponding *zinc, nickel,* and *cobalt* compounds have been prepared in a similar manner.

Manganese dithionate phenylhydrazine, $MnS_2O_6,5N_2H_3Ph$, obtained by adding phenylhydrazine to a 20 per cent. solution of manganese dithionate at about 80°, crystallises in thin, rhomboidal plates and resembles the preceding compound in its behaviour towards solvents. When heated, it begins to decompose at 125°, but does not melt below 250°. The corresponding zinc and cadmium compounds are obtained by double decomposition.

Zinc hypophosphite phenylhydrazine, $Zn(PO_2H_2)_2,2N_2H_3Ph$, prepared by adding phenylhydrazine to a boiling 15 per cent. solution of zinc hypophosphite, crystallises in rhomboidal plates, and is slightly soluble in cold water and insoluble in cold, slightly soluble in hot, alcohol. The *nickel* salt, $Ni(PO_2H_2)_2,2N_2H_3Ph$, is formed when phenylhydrazine is added to a cold 10 per cent. solution of nickel hypophosphite and crystallises in greenish-blue, rhomboidal plates. When heated, it becomes yellow at 170°, but does not melt or suffer much decomposition below 250°. It is slightly soluble in cold, and rather more soluble in hot, water, very slightly soluble in alcohol.

Compounds of phenylhydrazine with silver nitrate and with the borates, selenates, and pyrophosphates of the metals of the magnesium group have also been obtained and will shortly be described.

N. L.

Conversion of Phenylhydrazine into Diazobenzene. By EUGEN BAMBERGER (*Ber.*, 1899, **32**, 1808).—This conversion is readily brought about by the aid of mercuric acetate, and α-naphthylamine may be used as indicator for the diazo-salt which is formed.

J. J. S.

Paranitrophenylhydrazine Derivatives. By ELLIS HYDE (*Ber.*, 1899, **32**, 1810—1818. Compare this vol., i, 666).—*Paranitrophenylhydrazine picrate*, $C_{12}H_{10}N_6O_9$, crystallises in red needles melting at 119—120°, is insoluble in benzene or light petroleum, but dissolves in hot water, alcohol, or acetone. *β-Formoparanitrophenylhydrazide*, $NO_2 \cdot C_6H_4 \cdot NH \cdot NH \cdot CHO$, crystallises in straw-coloured needles melting at 182°, is readily soluble in the usual solvents, and also in sodium hydroxide solution. The β-acetyl compound melts at 205·5—206° (compare Abstr., 1893, i, 534), its *sodium* derivative forms a red powder; the *β-benzoyl* derivative, obtained by the action of benzoic anhydride on the base, crystallises in straw-coloured needles melting at 193°, and is sparingly soluble in benzene, toluene, or hot water.

A *triacetyl* derivative, $NO_2 \cdot C_6H_4 \cdot NAc \cdot NAc_2$, may be obtained by the action of acetic anhydride and sodium acetate on the base at 170—180°; it crystallises in long, colourless, glistening needles melting at 179—180, and dissolves in the usual solvents; when hydrolysed with dilute alkali, it yields the monacetyl derivative described above.

β-Acetodimethylparanitrophenylhydrazide, $NO_2 \cdot C_6H_4 \cdot NMeAc$, obtained by the action of sodium methoxide and methylic iodide on the monacetyl derivative, crystallises from alcohol in small, yellowish needles melting at 160—161°. All attempts to prepare a monomethyl derivative were unsuccessful.

Paranitrophenylsemicarbazide, $NO_2 \cdot C_6H_4 \cdot NH \cdot NH \cdot CO \cdot NH_2$, obtained by the action of potassium cyanate on paranitrophenylhydrazine hydrochloride, crystallises in small, yellowish needles melting and decomposing at 211—212°, and only sparingly soluble in benzene, toluene, or light petroleum.

Acetaldehyde paranitrophenylhydrazone, $NO_2 \cdot C_6H_4 \cdot NH \cdot N:CHMe$, crystallises in dark, golden-yellow needles melting at 128·5°, and is readily soluble in most solvents, with the exception of light petroleum.

Paranitrophenylhydrazones have been obtained from the following aldehydes and ketones: *Benzaldehyde*—red crystals melting at 90°, and sparingly soluble in sodium hydroxide. *Metanitrobenzaldehyde*—orange-red, glistening plates melting at 247°, and sparingly soluble in most solvents, with the exception of acetone. *Paranitrobenzaldehyde*—flat, reddish-violet, glistening needles melting at 249°. *Acetophenone*—orange-red, glistening needles melting at 184—185°, and readily soluble in most solvents. *Benzophenone*—sulphur-yellow, felted needles melting at 154—155°, and insoluble in aqueous sodium hydroxide. *Cinnamaldehyde*—orange-yellow crystals melting at 195°. *Pyruvic acid*—sulphur-yellow powder melting at 219—220°, and sparingly soluble in benzene, light petroleum, or chloroform.

Benzilparanitrophenylosazone, $C_2Ph_2(N \cdot NH \cdot C_6H_4 \cdot NO_2)_2$, forms a yellow, crystalline powder melting at 290°, and is sparingly soluble in the usual solvents, but dissolves readily in pyridine or nitrobenzene.

Phenanthraquinoneparanitrophenylhydrazone,

$$C_6H_4 \underset{C_6H_4}{\overset{CO}{<}} C:N \cdot NH \cdot C_6H_4 \cdot NO_2,$$
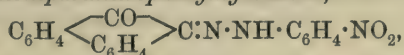
crystallises from xylene in red needles melting at 245°.

The paranitrophenylosazones of several sugars may be obtained by warming acetic acid solutions of the respective sugars and the base; in most cases, the yield is theoretical. They are best purified by solution in pyridine and precipitation with ether, all have a red colour, and are insoluble in all the usual solvents. Among the products formed in their preparation are always nitrobenzene, paranitraniline, and acetylparanitrophenylhydrazine. The following are the melting points: *glucosazone*, 257° (decomposes); *maltosazone*, 261° (decomposes); *lactosazone*, 258° (decomposes).

The product obtained by Bamberger and Sternitzky (Abstr., 1893, i, 522) from paranitrophenylhydrazine, acetone, and zinc chloride is 2 : 4-dichloraniline. The same product is formed when hydrazine sulphate, chloronitrobenzene, and zinc chloride are heated at 185°. Parachloraniline is formed when paranitrophenylhydrazine hydro-

chloride is heated with concentrated hydrochloric acid at 200°, whilst
with dilute hydrochloric acid (1 : 1) at 120—130° the products are
nitrobenzene, paranitraniline, and the unaltered base.   J. J. S.

Action of Phenylhydrazine on Chloranilic Acid. By HENRI
IMBERT and A. DESCOMPS (*Bull. Soc. Chim.*, 1899, [iii], 21, 72—74).
—When chloranilic acid and phenylhydrazine react in absolute
alcoholic solution, a *compound* is obtained isomeric with that produced
when 80 per cent. alcohol is employed (this vol., i, 205). The new
substance is colourless, and may be converted into the brown isomeride
by treating it with 90 per cent. alcohol, but the inverse change has
not been effected.   G. T. M.

Action of Hydrazines on Chloranilic and Bromanilic Acids.
By A. DESCOMPS (*Bull. Soc. Chim.*, 1899, [iii], 21, 366—368).—
Bromanilic acid resembles chloranilic acid (this vol., i, 205) in reacting
with phenylhydrazine in alcoholic solution to form a *compound*,
$C_6Br_2O_2(OH)_2,2N_2H_3Ph$, which crystallises in red needles, and is con-
verted by the action of 90 per cent. alcohol into a brownish-violet
isomeride. The action of hydrazine hydrate on bromanilic acid,
however the conditions may be varied, leads to the formation of only
one compound, a brick-red, crystalline *substance* of the composition
$C_6Br_2O_2(OH)_2,2N_2H_4$. The same applies to the action of hydrazine
hydrate on chloranilic acid.   N. L.

Paracetamidoformazylbenzene. By EDGAR WEDEKIND (*Ber.*,
1899, 32, 1918—1920).—*Paracetamidoformazylbenzene*,

$$NHPh \cdot N{:}CPh \cdot N_2 \cdot C_6H_4 \cdot NHAc,$$
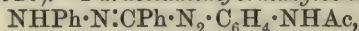
prepared by the action of paracetamidodiazonium chloride on
benzaldehydephenylhydrazone, is a reddish-black, crystalline powder,
which melts at 212—213° and dissolves readily in acetone or acetic
acid. Attempts to remove the acetyl group by hydrolysing with acids
or alkalis gave no definite results. When suspended in alcoholic
hydrogen chloride, it is readily oxidised by nitrous anhydride, the
colour changing from red to yellowish-brown; on diluting with water
and adding potassium iodide, *paracetamidotriphenyltetrazolium iodide*,

$$C_6H_5 \cdot C\!\!<^{N \cdot NPh}_{N{:}NI \cdot C_6H_4 \cdot NHAc},$$ is thrown down as a yellow precipitate,

which, when crystallised from hot water, melts at 289°; alkaline re-
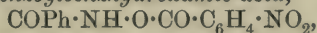ducing agents convert it into the original formazyl-compound.

The *α-metanitrophenylhydrazone* of *ethylic αβ-diketobutyrate*,

$$CH_3 \cdot CO \cdot C(COOEt){:}N_2H \cdot C_6H_4 \cdot NO_2,$$

crystallises from hot dilute alcohol and melts at 129—131°; the free
acid is canary-yellow, melts between 170° and 175°, and gives an
orange-yellow precipitate with phenylhydrazine.   T. M. L.

Isomeric Change in the Benzhydroxamic Acid Group. By
ALFRED WERNER and W. SKIBA (*Ber.*, 1899, 32, 1654—1666. Com-
pare Abstr., 1894, i, 585).—By the action of silver metachlorobenzoate
on benzhydroximic chloride, a small amount of benzildioxime peroxide,

$$N\!\!<^{CPh \cdot CPh}_{O \quad\quad O}\!\!>N,$$ is produced, the chief product being *metachloro-*

benzoylbenzhydroxamic acid, OH·CPh:N·O·CO·C$_6$H$_4$Cl or
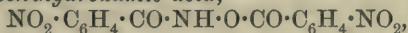$$\text{COPh·NH·O·CO·C}_6\text{H}_4\text{Cl};$$
this separates from alcohol in prismatic crystals, melts at 156°, and
is also prepared synthetically from benzhydroxamic acid and meta-
chlorobenzoic chloride. The intermediate product is probably meta-
chlorobenzoylbenzhydroximic acid, NOH:CPh·O·CO·C$_6$H$_4$Cl, but this
could not be isolated, as it immediately changes in the normal manner
into the isomeric hydroximic acid on the one hand and into benzil-
dioxime peroxide and metachlorobenzoic acid on the other.

The action of silver metanitrobenzoate on benzhydroximic chloride
gives benzildioxime peroxide and metanitrobenzoic acid, but the chief
product is *metanitrobenzoylbenzhydroxamic acid*,
$$\text{COPh·NH·O·CO·C}_6\text{H}_4\text{·NO}_2,$$
which crystallises from benzene, melts at 151°, and is also prepared
from benzhydroxamic acid and metanitrobenzoic chloride; the inter-
mediate hydroximic acid could not be isolated. *Paranitrobenzoyl-
benzhydroxamic acid* separates from methylic alcohol in glistening
crystals, and melts at 172°, whilst *orthonitrobenzoylbenzhydroxamic
acid* melts at 131—132°; these were obtained in the same way as
the metanitro-acid, but in the case of the paranitro-compound the
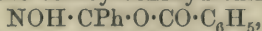benzildioxime peroxide forms the principal product of the reaction.

The chief products of the action of silver metanitrobenzoate on
metanitrobenzhydroximic chloride are metanitrobenzoic acid and
metanitrobenzildioxime peroxide, melting at 182—184°; *metanitro-
benzoylmetanitrobenzhydroxamic acid*,
$$\text{NO}_2\text{·C}_6\text{H}_4\text{·CO·NH·O·CO·C}_6\text{H}_4\text{·NO}_2,$$
is also produced in smaller quantity; it melts at 153—156°, and is
also prepared by the action of metanitrobenzoic chloride on metani-
trobenzhydroxamic acid; the intermediate hydroximic acid could not be
isolated. *Metanitrobenzhydroxamic acid* crystallises from alcohol and
melts at 151°. The interaction of silver benzoate and metanitro-
benzhydroximic chloride gives metadinitrobenzildioxime peroxide and
benzoic acid as the chief products, together with a small amount of
benzoylmetanitrobenzhydroxamic acid which melts at 153°, and is
prepared synthetically from benzoic chloride and metanitrobenzhydrox-
amic acid.

The interaction of silver paranitrobenzoate and paranitrobenz-
hydroximic chloride gives only paradinitrobenzildioxime peroxide and
paranitrobenzoic acid. *Paranitrobenzhydroxamic acid* crystallises from
alcohol and melts at 177°; *paranitrobenzoylparanitrobenzhydroxamic
acid* crystallises from alcohol in glistening needles and melts at
173—176°. The action of silver benzoate on paranitrobenzhydroximic
chloride gives paranitrobenzildioxime peroxide and benzoic acid as the
only products. *Benzoylparanitrobenzhydroxamic acid* crystallises from
alcohol in fine, colourless flakes and melts at 178°.

It will be seen that the benzoylbenzhydroximic acid,
$$\text{NOH·CPh·O·CO·C}_6\text{H}_5,$$
isolated as the first product of the interaction of silver benzoate and
benzhydroximic chloride (*loc. cit.*), becomes unstable on the intro-
duction of a chlorine atom or a nitro-group into either benzene
nucleus. Benzoylbenzhydroximic acid passes almost completely into

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the isomeric hydroxamic acid and only a small quantity breaks down into benzildioxime peroxide and benzoic acid ; in the interaction of a substituted silver benzoate on benzhydroximic chloride, however, the proportion of the dioxime peroxide is materially increased, and it becomes the chief product when metanitrobenzhydroximic chloride is used, and the only product in the case of paranitrobenzhydroximic chloride.   T. M. L.

Action of Zinc Ethyl on the so-called Nitramines and Isonitramines. By ARTHUR HANTZSCH (*Ber.*, 1899, **32**, 1722—1723).— On mixing ethereal solutions of zinc ethyl and phenylnitramine, the additive *compound*, $PhN_2O_2H + 4ZnEt_2$, is precipitated as a white, crystalline substance, fairly stable in air but decomposed on acidifying and extracting with ether, when the original nitramine is recovered. Phenylisonitramine (nitrosophenylhydroxylamine) gives an additive *compound*, $PhN_2O_2H + 2ZnEt_2$, which is also decomposed by dilute acids, giving rise to the original nitramine. Benzylisonitramine also gives an additive compound with zinc ethyl, but the isomeric benzylic ethers derived from it as well as methylic phenylisonitramine are not acted on. These results are taken as indicating that the so-called nitramines, like the isonitramines, are probably hydroxylic compounds, and not true nitramines.

With reference to Lachman's statement (this vol., i, 326), the author never questioned the existence of triethylamine oxide, but merely the fact of its boiling without decomposition.   T. M. L.

Symmetrical Dinitrodiphenylcarbamides. By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], **21**, 148—158).—*Diparanitrodiphenyl-carbamide*, $CO(NH \cdot C_6H_4 \cdot NO_2)_2$, prepared by heating phenylic carbonate (1 mol.) with paranitraniline (2 mols.) for 3 hours at 200°, crystallises from boiling alcohol in yellow, silky needles, and sublimes at about 310° without melting ; it is insoluble in water, benzene, chloroform, acetone, or ether, slightly soluble in boiling alcohol, more soluble in boiling nitrobenzene. When reduced with tin and hydrochloric acid, it yields a stannic derivative which is converted by treatment with hydrogen sulphide into the hydrochloride of diparamidodiphenylcarbamide, $CO(NH \cdot C_6H_4 \cdot NH_2)_2$, from which the base is liberated by ammonia. Fleischer and Nemes (this Jour., 1877, ii, 886) prepared this base by reducing the tetranitrodiphenylcarbamide, obtained by the nitration of diphenylcarbamide, and since paraphenylenediamine was found to be simultaneously produced they inferred the formation of tetranitroazoxybenzene in the nitration of diphenylcarbamide. This hypothesis is now shown to be unfounded, since paraphenylenediamine is also produced in the reduction of the pure dinitrodiphenylcarbamide prepared in the manner described above.

Dimetanitrodiphenylcarbamide has been obtained by several observers, but the melting points assigned to it have varied greatly. As obtained by the action of phenylic carbonate on metanitraniline, it crystallises either in white needles or in yellow plates, the former modification changing into the latter when heated at 190°, and finally melting sharply at 242°. Both modifications, when reduced with tin and hydrochloric acid, yield one and the same stannochloride,

$C_{13}H_{14}N_4O,2HCl,2SnCl_2 + 2\frac{1}{2}H_2O$, which crystallises in long, white, silky needles, and is converted by treatment with hydrogen sulphide into *dimetamidodiphenylcarbamide*, which crystallises in small, white needles melting at 208—209°. The isomerism observed with dimetanitrodiphenylcarbamide does not therefore extend to its derivatives.

Diorthonitrodiphenylcarbamide, $CO(NH \cdot C_6H_4 \cdot NO_2)_2$, could not be prepared by the action of phenylic carbonate on orthonitraniline, but was readily obtained by heating orthonitraniline with carbonyl chloride in a sealed tube at 130°; it forms yellow crystals melting at 225°, and yields a stannochloride which is converted by the action of hydrogen sulphide into *diorthamidodiphenylcarbamide*, which crystallises in slender, white needles melting and subliming at 243—245°.

<div align="right">N. L.</div>

Symmetrical Chloro-, Bromo-, and Iodo-diphenylcarbamides. By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 302—306).— These compounds can be obtained by heating the corresponding halogenated anilines (2 mols.) with phenylic carbonate.

Paradichlorodiphenylcarbamide, prepared by heating parachloraniline (2 mols.) with phenylic carbonate (1 mol.) for two hours at 200°, forms white needles, melts and sublimes at 306—307°, and is readily soluble in boiling glacial acetic acid, less so in boiling alcohol, and insoluble in water, ether, benzene, or chloroform.

Metadichlorodiphenylcarbamide, $CO(NH \cdot C_6H_4Cl)_2$, crystallises in small, white needles melting at 245°, and dissolves in hot glacial acetic acid or alcohol, and to a slight extent in cold alcohol, but is insoluble in water, ether, benzene, or chloroform.

Orthodichlorodiphenylcarbamide forms small, white needles melting at 235—236°, and is insoluble in water, benzene, ether, or chloroform, but is dissolved by hot alcohol or glacial acetic acid.

Paradibromodiphenylcarbamide forms thin, white plates which, on heating, do not melt, but sublime unchanged at 330°.

Metadibromodiphenylcarbamide forms white needles melting at 263°, and dissolves in hot alcohol or glacial acetic acid, but is insoluble in water and the neutral organic solvents.

Orthodibromodiphenylcarbamide crystallises in small, white needles which melt at 219—220°, and is soluble in hot alcohol or acetic acid, but insoluble in water, benzene, or chloroform.

These carbamide derivatives can also be obtained by the action of phosgene on haloid derivatives of aniline. *Paradi-iododiphenylcarbamide*, $CO(NH \cdot C_6H_4I)_2$, so obtained, forms thin, white needles which sublime without melting at above 300°, and is insoluble in all the ordinary organic solvents except boiling glacial acetic acid, which dissolves it only slightly; it does not lose its iodine even when boiled with concentrated nitric or nitrohydrochloric acid, but on calcining it with excess of quicklime, the iodine is removed. This compound can not be obtained by heating pariodaniline with phenylic carbonate, as decomposition takes place with the formation of a tarry mass and the liberation of large quantities of iodine. <div align="right">T. H. P.</div>

Chlorination of Hydrobenzamide. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1899, [iii], 21, 10—11).—By the chlorination of hydro-

benzamide, Müller, in 1859, obtained a viscid oil which had the composition $C_{21}H_{18}N_2Cl_4$; this substance, on heating at 180—220°, evolved hydrogen chloride and yielded a liquid boiling at 187° which had a composition corresponding with $C_{21}H_{17}ClN_2$. The author finds that this product is in reality a mixture of benzonitrile (2 mols.) and benzylic chloride (1 mol.), the former constituent being separated and identified by its compound with hexamethylenetetramine, and the latter by hydrolysis to benzoic acid. The viscid oil is an additive compound whose constitution may be represented by the formula $CHPhCl \cdot NCl \cdot CHPh \cdot N:CHPh$. G. T. M.

Synthesis of Aromatic Thioanilides. By LUDWIG GATTERMANN [and in part FRIEDMANN, KNÜTTEL, VON KÜYLENSTJERNA, J. A. RÖLOF-SEN, F. SCHAAR-ROSENBERG, TETZLAFF, TUST, and ZIMMER] (*J. pr. Chem.*, 1899, ii,**59**, 572—594).—Thiocarbimides condense with aromatic hydrocarbons and phenolic ethers in the presence of aluminium chloride to form aromatic thioanilides. The reaction takes place in two stages. Hydrogen chloride which is always present when aluminium chloride is used, combines with the thiocarbimide, forming the unstable chloride of a thiocarbamic acid, which then reacts with the hydrocarbon or phenolic ether to form the thioanilide. The thioanilides are well characterised substances, but are only hydrolysed with difficulty, heating in a sealed tube at 180° with dilute sodium carbonate for five hours being recommended as the best method.

The following rules hold in this synthesis, (I) with homologues of benzene the $-CS \cdot NHPh$ group takes up a para-position to an alkyl group. (II) Similarly, phenolic ethers give parathioanilides. (III) With homologues of phenolic ethers, it is the ether group, and not the alkyl group, which determines the position of the $-CS \cdot NHPh$ group. (IV) If the para-position to the ether group in a phenolic ether is occupied by an alkyl group, the $-CS \cdot NHPh$ group takes up the ortho-position. In general, on treating the thioanilides with iodine in alcoholic solution, the sulphur is replaced by oxygen.

On oxidation with potassium ferricyanide, the thioanilides give ring compounds of the type $CPh\lessgtr^S_N > C_6H_4$. Benzene and phenylthio-carbimide give a poor yield of thiobenzanilide; by the action of aluminium chloride on the phenylthiocarbimide, a secondary product melting at 154° is obtained, which is identical with that obtained by the action of bromine on the phenylthiocarbimide (Proskauer and Sell, Abstr., 1877, i, 67).

Phenylthiocarbimide and toluene give *thioparatoluanilide*, which forms long, bright yellow needles, melts at 140—141°, and yields paratoluic acid on hydrolysis. The *thioanilide* from orthoxylene and phenylthiocarbimide forms yellow prisms, melts at 106—107°, and gives 3 : 4-dimethylbenzoic acid on hydrolysis. In similar manner, meta-xylene gives 2 : 4-*dimethylthiobenzanilide*, crystallising from alcohol in the form of pale yellow prisms melting at 106·5—107·5°. Toluene and tolylthiocarbimide yield the *paratoluidide* of *parathiotoluic acid*, which forms large, yellow crystals melting at 165—166°; this on hydrolysis gives paratoluic acid, and on treatment with iodine, paratoluic para-

toluidide. As a bye-product, the sulphide of paratolylthiocarbimide is obtained, which crystallises from glacial acetic acid in the form of bright yellow needles melting at 183—184°.

Anisoil and phenylthiocarbimide yield *paramethoxythiobenzanilide*, which crystallises in long, bright yellow needles, and melts at 153—154°; on oxidation, this yields colourless needles melting at 134—135°. Phenetoil and phenylthiocarbimide yield *paraphenoxy-4-thiobenzanilide*, which forms long, bright yellow needles melting at 143°; the product obtained from it by oxidation forms colourless leaflets melting at 120°. Orthotolylic methylic ether and phenylthiocarbimide give *paramethoxymetamethylthiobenzanilide*, crystallising in yellow needles and melting at 177°. *Parethoxymetamethylthiobenzanilide* forms long, yellow needles and melts at 169°, and the corresponding *parethoxymetamethylbenzoic acid*, obtained by its hydrolysis, forms colourless needles melting at 199°.

Paramethoxyorthomethylthiobenzanilide forms yellow needles melting at 96°. *Parethoxyorthomethylthiobenzanilide* crystallises in yellow needles melting at 117°, and *parethoxyorthomethylbenzoic acid*, obtained by its hydrolysis, crystallises from water in colourless needles melting at 146°.

Parethoxytoluene and phenylthiocarbimide yield *4-ethoxy-5-methylthiobenzanilide*, which crystallises in yellow needles melting at 111°.

Thymylic methylic ether and phenylthiocarbimide yield *4-methoxy-2-methyl-5-isopropylthiobenzanilide*, which forms yellow, prismatic crystals and melts at 132—133°. *4-Ethoxy-2-methyl-5-isopropylthiobenzanilide*, forms yellow prisms and melts at 147—148°.

With phenylthiocarbimide, resorcinol diethylic ether yields 2 : 4-*diethoxythiobenzanilide*, which crystallises in yellow needles and melts at 121°; diphenylic ether yields *paraphenoxythiobenzanilide*, which forms yellow scales melting at 133°.

Phenylthiocarbimide, with 1-methoxynaphthalene, gives a thioanilide crystallising from glacial acetic acid in the form of yellow prisms melting at 179°; with 1-ethoxynaphthalene, a thioanilide in the form of yellow needles from glacial acetic acid melting at 199—200°; with 2-methoxynaphthalene and 2-ethoxynapthalene, thioanilides crystallising from alcohol in the form of flat, yellow crystals melting respectively at 141° and 164—165°. Attempts to hydrolyse these compounds were unsuccessful, and their constitution is doubtful.

Phenylthiocarbimide gives with orthochlor-, brom-, and iod-anisoil respectively, 3-*chloro-4-methoxythiobenzanilide*, which forms yellow plates melting at 205°, 3-*bromo-4-methoxythiobenzanilide*, which crystallises in flat, yellow needles melting at 204°, and 3-*iodo-4-methoxythiobenzanilide*, which forms yellow needles melting at 206·5°; with orthochlorophenetoil, 3-*chloro-4-ethoxy-thiobenzanilide*, which forms broad, yellow needles melting at 195·5° is obtained.

Diphenylic ethylenic ether and phenylthiocarbimide give a thioanilide of the formula $C_2H_4(O\cdot C_6H_4\cdot CS\cdot NHPh)_2$, forming lustrous, yellow plates and melting at 255°.

Orthotolylthiocarbimide yields, with anisoil, *paramethoxythiobenzorthotoluidide*, which forms yellow needles melting at 95°; with phenetoil, *parethoxythiobenzorthotoluidide* is obtained in yellow needles melting at 106°; with orthotolylic ethylic ether, 4-*ethoxy-3-methylthiobenzorthotoluidide* is obtained as yellow needles melting at 137°.

Metatolylthiocarbimide yields, with anisoil, *paramethoxythiobenzo-metatoluidide*, which crystallises in yellow needles melting at 125°; with phenetoil, *parethoxythiobenzometatoluidide* is obtained as yellow needles melting at 130°.

Paratolylthiocarbimide gives, with anisoil, *paramethoxythiobenzo-paratoluidide*, which forms yellow needles melting at 157°; with phenetoil, *parethoxythiobenzoparatoluidide* is obtained; it forms yellow needles melting at 151°; with orthotolylic ethylic ether, 4-*ethoxy-3-methylthiobenzoparatoluidide* is obtained, crystallising in yellow needles and melting at 185°.

Metaxylylthiocarbimide gives, with phenetoil, *parethoxythiobenzo-metaxylidide*, which forms flat, yellow crystals melting at 139—140°; with orthotolylic ethylic ether, 4-*ethoxy-3-methylthiobenzometaxylidide* is obtained as yellow needles melting at 132—133°.

Pseudocumylthiocarbimide (? which), with orthotolylic ethylic ether, gives a thioanilide of the formula $OEt \cdot C_6H_3Me \cdot CS \cdot NH \cdot C_6H_2Me_2$ [1 : 2 : 4], which forms yellow needles melting at 143°.

Paranisylthiocarbimide gives, with anisoil, *paramethoxythiobenzo-paranisidide*, which forms small, yellow needles melting at 148°; with phenetoil, *parethoxythiobenzoparanisidide* is obtained, crystallising in long, yellow needles melting at 154·5°.

Paraphenetylthiocarbimide, prepared from paraphenetidine and thio-phosgene, forms colourless leaflets melting at 62·5°; with anisoil, it yields *paramethoxythiobenzoparaphenetidide*, which forms yellow needles melting at 135·5°; with phenetoil, it yields *parethoxythiobenzopara-phenetidide*, which crystallises in small, yellow needles melting at 151—152°, and, with iodine, gives *parethoxybenzoparaphenetidide*, forming colourless needles melting at 171°, and with potassium ferri-cyanide, a colourless oxidation product melting at 163°.

Parachlorophenylthiocarbimide, with anisoil, gives *paramethoxythio-benzoparachloranilide*, which forms thick, yellow prisms melting at 182°; with phenetoil, *parethoxythiobenzoparachloranilide* is formed, crystallising in thick, yellow prisms melting at 194—195°; with orthotolylic ethylic ether, 4-*ethoxy-3-methylthiobenzoparachloranilide* is obtained as yellow prisms melting at 203°; with α-naphthylic methylic ether, 4-*methoxythionaphthoparachloranilide* is obtained, crystallising in bright yellow prisms melting at 205—206°; the corresponding *ethoxy*-compound forms small needles melting at 191—192°.

Metabromophenylthiocarbimide, prepared by adding metabromaniline to thiophosgene in chloroform solution, boils at 256°; with anisoil, it yields *paramethoxythiobenzometabromanilide*, which forms yellow needles melting at 150—151°; with phenetoil, the corresponding *ethoxy*-compound, melting at 139°, is obtained; with orthotolylic ethylic ether, 4-*ethoxy-3-methylthiobenzometabromanilide* is formed, crystallising in yellow needles and melting at 144°; with α-naphthylic methylic ether, 4-*methoxythionaphthometabromanilide* is obtained, crystallising in yellow needles and melting at 149—150°; the corresponding *ethoxy*-compound melts at 159—160°.

α-Naphthylthiocarbimide, with anisoil, gives *paramethoxythiobenzo-α-naphthalide*, which forms deep yellow prisms melting at 147—148°; the corresponding *ethoxy*-compound forms yellow prisms melting at 156—157°; with orthotolylic ethylic ether, it gives 4-*ethoxy-3-methyl-*

thiobenzo-α-naphthalide, which forms yellow needles and melts at 154—155°; with α-naphthylic methylic ether, it gives 4-*methoxythio-α-naphtho-α-naphthalide*, crystallising in bright, yellow needles and melting at 196—197°; the *ethoxy*-compound forms yellow needles melting at 144—145°.

Paramethoxythiobenzo-β-naphthalide forms yellow plates melting at 158—159°; the corresponding *ethoxy*-compound melts at 148—149°.

Metaphenylenedithiocarbimide, with anisoil, gives a compound forming small, yellow needles melting at 218—219°; the corresponding *ethoxy*-compound, prepared from phenetoil, is similar, and melts at 233°.

Paraphenylenedithiocarbimide, with anisoil and phenetoil, give similar compounds crystallising in yellow needles melting respectively at 281° and 293°.

Benzidinedithiocarbimide, prepared in a similar manner to meta-bromophenylthiocarbimide, melts at 203°; with anisoil and phenetoil, it gives compounds crystallising in yellow needles and melting at 302—303° and 293° respectively.

Orthotolidinedithiocarbimide, with anisoil, gives the compound $C_{12}H_6Me_2(NH\cdot CS\cdot C_6H_4\cdot OMe)_2$, which crystallises in yellow needles melting at 250—252°; the corresponding *ethoxy*-compound melts at 235—236°.

Dianisyldithiocarbimide, prepared by the action of thiophosgene on dianisidine, crystallises in yellowish leaflets melting at 192—194°, and, with anisoil, condenses to form a compound,

$$C_{12}H_6(OMe)_2(NH\cdot CS\cdot C_6H_4\cdot OMe)_2,$$
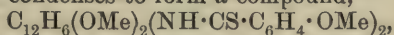
which crystallises in yellow needles melting at 222—224°; the *ethoxy*-compound, prepared from phenetoil, forms leaflets melting at 233—235°.

The yields in all cases are good, with the one exception of that from benzene and phenylthiocarbimide.　　　　　R. H. P.

Action of Thiocarbanilide on Acid Anhydrides. By FREDERICK L. DUNLAP (*Amer. Chem. J.*, 1899, 21, 528—530. Compare Abstr., 1897, i, 471).—By heating together molecular proportions of thio-carbanilide and succinic anhydride, the products previously obtained were succinanil, carbon oxysulphide, and aniline, but by keeping the temperature at 95—96°, the products are phenylthiocarbimide and succinanilic acid melting at 144·5—145·5°. The intermediate additive product, which could not be obtained in this case, was isolated when maleic anhydride was used in place of succinic anhydride. *Diphenyl-thiomaleuric acid*, $COOH\cdot CH\colon CH\cdot CO\cdot NPh\cdot CS\cdot NHPh$, crystallises from alcohol in short, flat, transparent prisms and melts at 160°; it is readily soluble in acetone, very sparingly so in ether or chloroform, and insoluble in benzene, light petroleum, carbon bisulphide, or water; it forms crystalline, barium, calcium, silver, potassium, and sodium salts. When the temperature is raised to 180°, the mixture begins to liberate carbon oxysulphide, and the gas is still more rapidly evolved when the temperature is raised to 200° or above.

　　　　　　　　　　　　　　　　　　　　　　T. M. L.

Nitrovanillin. By WALTHER VOGL (*Monatsh.*, 1899, 20, 383—400). —β-*Nitrovanillin* or 5-*nitro*-4-*hydroxy*-3-*methoxybenzaldehyde*, prepared

by the action of nitric acid saturated with nitrous acid on an ethereal solution of vanillin at 10°, separates from boiling glacial acetic acid in pale yellow, crystalline nodules, melts at 172°, is almost insoluble in water, rather more soluble in boiling alcohol or ether, and easily soluble in hot glacial acetic acid. It dissolves in dilute aqueous solutions of the hydroxides or carbonates of the alkalis, forming yellow solutions. The potassium salt resembles potassium dichromate in appearance. The *acetyl* derivative separates in pale yellow crystals and melts at 88°. The *oxime* crystallises from boiling alcohol in lustrous, yellow needles, melts at 200—201°, and is almost insoluble in water, but easily soluble in ether and alcohol. By the action of acetic anhydride on the oxime, *nitracetoxymethoxybenzonitrile,*

$$[CN : OMe : OAc : NO_2 = 1 : 3 : 4 : 5],$$
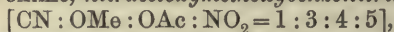
is formed ; it separates from alcohol as a white, crystalline mass with a tinge of yellow, melts at 102°, is easily soluble in ether, ethylic acetate, or glacial acetic acid, and less so in benzene. The corresponding acid, *nitrohydroxymethoxybenzoic acid,* or β-*nitrovanillic acid*, prepared by hydrolysing the nitrile, crystallises from glacial acetic acid in small, yellow leaflets often grouped in rosette-like clusters, melts at 209—210° without decomposing, and is sparingly soluble in hot water but easily so in alcohol. This compound is apparently not identical with Tiemann's nitrovanillic acid (this Journal, 1876, ii, 524). The corresponding β-*amidovanillic acid*, obtained by reducing the nitro-acid with tin and hydrochloric acid, separates as the hydrochloride in white, lustrous scales, becomes coloured at 200°, but does not melt below 250°, is easily soluble in alcohol and ether, and yields a platino-chloride, $2C_8H_7O_4 \cdot NH_2, H_2PtCl_6$. The *acetyl* derivative melts at 215°. The chloride of *methoxyhydroxydiazobenzoic acid,*

$$[COOH : OMe : OH : N_2Cl = 1 : 3 : 4 : 5],$$
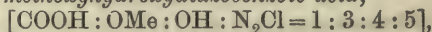
prepared by diazotising the amido-acid, crystallises from concentrated hydrochloric acid, decomposes with liberation of gas when gently heated, and is very sparingly soluble in water. When boiled with a very dilute solution of sodium carbonate in water, it forms *methoxygallic acid*, $[COOH : OMe : (OH)_2 = 1 : 3 : 4 : 5]$, and vanillic acid. The former crystallises from xylene in yellowish-white needles, melts at 199—200°, is easily soluble in boiling water, and soluble in alcohol or ethylic acetate ; with ferric chloride, the aqueous solution gives a bluish-black coloration, which, on the addition of sodium carbonate, becomes first violet and then bluish-red. The vanillic acid, which melts at 206°, probably results from the formation of a dicarboxylic acid by the replacement of the diazo-group by carboxyl and the subsequent loss of carbonic anhydride by this acid. Attempts to obtain an amido-product from nitrovanillin by reducing it with tin and hydrochloric acid or with stannous chloride resulted for the most part in the formation of unstable or tarry products. E. W. W.

Action of Parachloro- and Parabromo-phenyl Bromomethyl Ketones on Aniline. By A. COLLET (*Bull. Soc. Chim.*, 1899, [iii], 21, 65—67. Compare Abstr., 1898, i, 123, 139, 447).— *Parachlorophenyl anilidomethyl ketone*, $C_6H_4Cl \cdot CO \cdot CH_2 \cdot NHPh$, obtained by heating together aniline and parachlorophenyl bromomethyl ketone in alcoholic solution, crystallises from alcohol and chloroform

in bright yellow needles melting at 187—188°; when the ketone is added to boiling aniline, 1'-*parachlorophenylindole*,

$$C_6H_4 \diagup_{NH}^{CH} \diagdown C \cdot C_6H_4Cl,$$
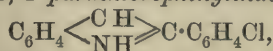
is produced; this crystallises from alcohol in colourless leaflets and melts at 201—202° (compare Bischler, Abstr., 1892, 1465; Kunckell, Abstr., 1897, i, 282).

Parabromophenyl anilidomethyl ketone melts at 119—120°; 1'-*para-bromophenylindole* melts at 208—209°; these compounds resemble the corresponding chloro-derivatives. G. T. M.

Parabromophenyl Methyl Ketone. By A. Collet (*Bull. Soc. Chim.*, 1899, [iii], 67—68).—*Parabromophenyl methyl ketoxime*,

$$C_6H_4Br \cdot CMe \dot{:} NOH,$$
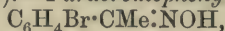
crystallises from alcohol in long, colourless needles and melts at 128°; when heated at 100° with concentrated sulphuric acid, it is converted into parabromacetanilide. When parabromophenyl methyl ketone is treated with bromine (1 mol.), parabromophenyl bromomethyl ketone is produced, and this substance, when oxidised with alkaline potassium permanganate, yields parabromophenylglyoxylic acid, $C_6H_4Br \cdot CO \cdot COOH$ (Rupe, Abstr., 1892, i, 218).

Parabromophenyl dibromomethyl ketone, $C_6H_4Br \cdot CO \cdot CHBr_2$, is obtained when 2 mols. of bromine are employed; it separates from alcohol in colourless crystals melting at 92—93°, is oxidised by permanganate to parabromobenzoic acid, and when treated with excess of potash, parabromophenylglycollic acid, $C_6H_4Br \cdot CH(OH) \cdot COOH$, is produced. G. T. M.

Parachlorophenyl Methyl Ketone. By A. Collet (*Bull. Soc. Chim.*, 1899, [iii], 21, 68—70).—Parachlorophenyl methyl ketone is most readily prepared by mixing together acetic chloride, chlorobenzene, and aluminium chloride, a yield of 55 per cent. being obtained. The *oxime*, $C_6H_4Cl \cdot CMe \dot{:} NOH$, crystallises in colourless needles melting at 95°, and on treatment with warm concentrated sulphuric acid is converted into parachloracetanilide. The *phenylhydrazone* crystallises in yellow needles and melts at 114°. Parachlorophenyl bromomethyl ketone is prepared by adding bromine (1 mol.) to parachlorophenyl methyl ketone dissolved in carbon bisulphide, and is identical with that obtained from bromacetic chloride and chlorobenzene.

Parachlorophenylglyoxylic acid, $C_6H_4Cl \cdot CO \cdot COOH$, obtained by oxidising parachlorophenyl bromethyl ketone with permanganate, separates from alcohol in colourless crystals.

Parachlorophenyl dibromomethyl ketone, $C_6H_4Cl \cdot CO \cdot CHBr_2$, produced by adding bromine (2 mols.) to parachlorophenyl methyl ketone dissolved in carbon bisulphide, separates from alcohol in colourless crystals melting at 92·5°.

Parachlorophenylglycollic acid, $C_6H_4Cl \cdot CH(OH) \cdot COOH$, obtained by mixing the preceding compound with 10 per cent. caustic potash, crystallises from benzene in colourless needles melting at 112—113°. G. T. M.

Bromophenacetin. By WILHELM VAUBEL (*Ber.*, 1899, **32**, 1875). —A claim for priority.   T. M. L.

Orthohydroxyphenoxyacetic Acid and Orthophenylenedioxyacetic Acid. By CHARLES MOUREU (*Bull. Soc. Chim.*, 1899, [iii], **21**, 107—109).—The intense blue coloration produced on adding ferric chloride to a solution of orthohydroxyphenoxyacetic acid (see this vol., i, 679) disappears on neutralisation, and this fact is made use of in the alkalimetric estimation of the acid.

In the preparation of orthohydroxyphenoxyacetic acid by the condensation of chloracetic acid with catechol, *orthophenylenedioxydiacetic acid*, $C_6H_4(O \cdot CH_2 \cdot COOH)_2$, is also formed; this crystallises from boiling water in slender needles melting at 172—174°.   N. L.

Action of Sulphuryl Chloride on Alkylic Hydroxybenzoates. By GIROLAMO MAZZARA (*Gazzetta*, 1899, **29**, i, 340—347).—Ethylic 5-chlorosalicylate, $OH \cdot C_6H_3Cl \cdot COOEt$, obtained by the action of sulphuryl chloride on ethylic salicylate, crystallises in long, lustrous needles melting at 25°. Smith and Macchall (Abstr., 1878, 879) gave the melting point as 110°, although in both cases the products give rise to the same chlorosalicylamide melting at 223°. As methylic 5-chlorosalicylate melts at 48·5°, the lower temperature is probably correct for the ethylic salt, since the ethylic derivatives of such acids are, in general, more volatile than the corresponding methylic salts.

Ethylic 5-chloro-2-ethoxybenzoate, $OEt \cdot C_6H_3Cl \cdot COOEt$, prepared by heating under pressure a mixture of ethylic 5-chlorosalicylate, potassium hydroxide, and ethylic iodide in presence of absolute alcohol, boils at 226° under 55 mm. pressure, and when cooled by means of salt and snow, solidifies to a crystalline mass which liquefies at ordinary temperatures. Free *5-chloro-2-ethoxybenzoic acid*, obtained by hydrolysing the ethylic salt with 40 per cent. potash, crystallises from dilute alcohol in shining, white laminæ melting at 118°.

No trace of dichlorosalicylic acid is obtained by the action of an excess of sulphuryl chloride on ethylic salicylate.   T. H. P.

Derivatives of Ethylic Succinylsuccinate. By J. GUINCHARD (*Ber.*, 1899, **32**, 1742—1744. Compare Hantzsch and Zeckendorf, Abstr., 1888, 278; Hantzsch and Hermann, *ibid.*, 954; Böniger, *ibid.*, 954).—*Ethylic di-iodoquinoldicarboxylate*, $C_6I_2(OH)_2(COOEt)_2$, separates from benzene in colourless needles and melts at 167°. The crystals of the substance are always white, but solutions in benzene, ether, or chloroform are deep green, and only the alcoholic solution is colourless when cooled with a freezing mixture; the fused substance is also green before it begins to decompose, owing to the formation of the isodynamic quinonoid modification. *Ethylic di-iodoquinonedicarboxylate*, $C_6I_2O_2(COOEt)_2$ the product of oxidation with nitric acid in alcoholic solution, crystallises in small, orange-coloured needles, melts and decomposes at 231°, dissolves slightly in alcohol or ether, and readily in benzene. *Ethylic dipiperidoquinonedicarboxylate*, $C_6O_2(C_5H_{10}N)_2(COOEt)_2$, forms fine dark violet crystals, melts at 148°, dissolves readily in alcohol or benzene and slightly in water, does not form salts with acids, is

hydrolysed by sodium hydroxide to piperidine and ethylic dihydroxy-quinonedicarboxylate, and when reduced yields ethylic tetrahydroxy-terephthalate. *Ethylic ethylanilidoquinonedicarboxylate,*

$$C_6O_2(NPhEt)_2(COOEt)_2,$$
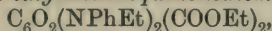
crystallises from alcohol in reddish-violet needles and melts at 182°.

Ethylic dibromoquinoldicarboxylate forms an *additive* compound with two mols. of zinc ethyl. **T. M. L.**

Action of Benzenesulphonic Chloride on Asymmetrical Alkylphenylhydrazines. By EUGEN BAMBERGER (*Ber.*, 1899, **32**, 1804—1805).—Hinsberg's method for the separation of primary and secondary amines by the aid of benzenesulphonic chloride cannot always be employed with success. For example, methylphenylhydrazine in addition to giving the normal monosulphonyl derivative,

$$NMePh \cdot NH \cdot SO_2Ph,$$
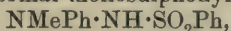
melting at 131·5—132° and soluble in alkali (*Ber.*, 1894, **27**, 372), also yields a *dibenzenesulphonylmethylphenylhydrazine*, $NMePh \cdot N(SO_2Ph)_2$, which crystallises in hard, glistening prisms melting at 169—170°, and is insoluble in alkali; the same compound is readily obtained when the monosulphonyl derivative is treated according to the Schotten-Baumann method with benzenesulphonic chloride. Ethyl-phenylhydrazine reacts in a similar manner, yielding a mixture of the *monobenzenesulphonyl* derivative soluble in alkali and melting at 96°, and of the *dibenzenesulphonyl* compound melting at 140—141° and insoluble in alkali. Benzenesulphonemethylphenylhydrazine, when shaken with benzoic chloride and alkali, yields the benzoyl derivative $NMePh \cdot NBz \cdot SO_2Ph$, melting at 119°. (Compare Solonina, *J. Russ. Chem. Soc.*, 1897, **29**, 404.) **J. J. S.**

The So-called Benzil Reaction. By EUGEN BAMBERGER and ROLAND SCHOLL (*Ber.*, 1899, **32**, 1809—1810).—The colour reaction for 1 : 2-diketones previously described (Bamberger, Abstr., 1885, 807) is not given by pure benzil, but is instantaneously produced when a minute quantity of benzoin is present. This reaction (the benzil-benzoin reaction) can therefore be made use of in testing for either benzil or benzoin. **J. J. S.**

Hydroxydiphenylene Ketone and Orthophenylsalicylic Acid. By GEORG HEYL (*J. pr. Chem.*, 1899, [ii], **59**, 434—463. Compare this vol., i, 216; also Staedel, Abstr., 1895, i, 233).—Sym-metrical diorthamidobenzophenone is best prepared by the reduc-tion with iron powder of symmetrical diorthonitrobenzophenone dissolved in glacial acetic acid, a small quantity of *symmetrical ortho-nitrorthamidobenzophenone* being obtained as a bye-product; this crystal-lises in yellow needles melting at 149—150°. The *sodium, potassium, ammonium,* and *silver* salts of hydroxydiphenyleneketone are described; the *sodium* salt crystallises from water in characteristic lustrous, reddish-yellow plates.

Orthophenylsalicylic acid, which crystallises from water and melts at 195°, can be distinguished from salicylic acid by its yielding a deep red liquid on treatment with cold concentrated sulphuric acid, from

which solution a yellow precipitate of hydroxydiphenylene ketone can be obtained on the addition of water. Under similar treatment, salicylic acid is recovered unchanged; further, the red coloration formed on adding hydrogen peroxide to a solution of sodium salicylate is not given by sodium orthophenylsalicylate.

The *silver* and *potassium* salts of orthophenylsalicylic acid are described. - R. H. P.

Imines of Benzophenone and the Constitution of Auramine. By Carl Graebe (*Ber.*, 1899, **32**, 1678—1783).—The substance prepared by the action of ammonia on 2 : 2'-dihydroxybenzophenone and formulated as $OH \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot NH_2$ (Abstr., 1892, 1227), is shown to be 2 : 2'-*dihydroxybenzophenonimine*, $NH\!:\!C(C_6H_4 \cdot OH)_2$, since it is hydrolysed by dilute hydrochloric acid to 2 : 2'-dihydroxybenzophenone and ammonia, and does not yield a diazo-compound.

As is shown in the following abstract and this vol., i, 705, aniline condenses directly at 195—200° with most derivatives of benzophenone which are substituted in one of the ortho-positions, giving rise to the corresponding benzophenonephenylimine derivative; 2 : 2'-dihydroxybenzophenone, however, loses a second molecule of water and gives xanthonephenylimine, $O{<}{C_6H_4 \atop C_6H_4}{>}C\!:\!NPh$. Condensation does not occur under these conditions with benzophenone, meta- and para-hydroxybenzophenone, meta- and para-chlorobenzophenone, orthonitrobenzophenone, orthamidobenzophenone and 4 : 4'-dihydroxybenzophenone.

Benzophenonephenylimine, $NPh\!:\!CPh_2$, is usually prepared from benzophenone chloride, but direct condensation occurs when benzophenone is heated at 240—250° in a flask with a long neck and three or four times its weight of aniline is gradually added from a dropping funnel. Under similar conditions, 4 : 4'-dihydroxybenzophenone also gives an orange-yellow phenylimine.

Benzophenone and all its derivatives are yellow and give yellow salts; with hydrogen sulphide, the phenylimine group is replaced by sulphur. Their behaviour is quite similar to that of auramine, and the latter is therefore regarded as a ketone-imine, $NH\!:\!C(C_6H_4 \cdot NMe_2)_2$. The salts of auramine are also regarded as ketone-imines, and not as quinonoid in structure (Stock, Abstr., 1893, i, 472), since the difference in colour between the base and its salts is only small, corresponding with that which exists between hydroxybenzophenone and its salts, and much less than that between acridine and its salts. Moreover, the quinonoid formula for auramine hydrochloride,

$$NMe_2 \cdot C_6H_4 \cdot C(NH_2)\!:\!C_6H_4\!:\!NMe_2Cl,$$
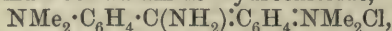
differs only from that of malachite-green in the replacement of $-C_6H_5$ by $-NH_2$, and the salts might therefore be expected to have a green to blue colour. Finally auramine hydrochloride is readily converted into phenylauramine by heating with aniline, but is not attacked by methylaniline, corresponding with the expression,

$${>}C\!:\!NH \rightarrow {>}C\!:\!NPh, \text{ and not with } {>}C \cdot NH_2 \rightarrow {>}C \cdot NMePh.$$
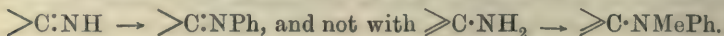
T. M. L.

Ortho-derivatives of Benzophenonephenylimine. By CARL GRAEBE and F. KELLER (*Ber.*, 1899, **32**, 1683—1688).—*Orthohydroxybenzophenonephenylimine*, OH·C₆H₄·CPh:NPh, crystallises in stout needles of an intense golden-yellow colour, melts at 138·5° (corr.), does not dissolve in water but dissolves readily in hot alcohol; it does not dissolve in aqueous alkalis, but remains in solution when a drop of soda is added to the alcoholic solution and an excess of water is then added; it dissolves in an 18 per cent. solution of hydrogen chloride, but is thrown down again unchanged on adding an excess of water. On heating with hydrochloric acid, or with water at 150°, it is decomposed into aniline and orthohydroxybenzophenone. The *acetyl* derivative crystallises from alcohol in colourless flakes and melts at 129°; its *hydrochloride* is a yellow salt; on boiling with water, it is decomposed into hydroxybenzophenone, acetic acid, and aniline. *Orthomethoxybenzophenonephenylimine* crystallises from alcohol in yellow needles and melts at 77°; its alcoholic solution is precipitated on adding soda and excess of water, but towards hydrochloric acid it behaves like the hydroxy-compound.

2 : 4′-*Dihydroxybenzophenonephenylimine* crystallises from alcohol in dark yellow needles and melts at 214°; it dissolves slowly in alkalis at ordinary temperatures, but loses aniline when heated; it forms a yellow *hydrochloride* which is decomposed on boiling with water; the molecular weight, determined from the freezing point of a solution in phenol, is normal. The *diacetyl* derivative is greenish-yellow, and forms a bright yellow *hydrochloride*.

2 : 3 : 4-*Trihydroxybenzophenonephenylimine* melts at 95°, is not soluble in water, but dissolves readily in alcohol and in alkalis to a yellow solution; 18 per cent. hydrochloric acid dissolves it, but the yellow solution is decomposed on boiling.

Orthochlorobenzophenone readily solidifies when pure and melts at 45·5°, it boils at 330° (corr.) and crystallises from a mixture of chloroform and light petroleum in well-formed tablets. *Orthochlorobenzophenonephenylimine* crystallises from alcohol in yellow needles, melts at 128° and dissolves readily in chloroform; it dissolves in moderately concentrated hydrochloric acid to a yellow solution, but on heating, the colour disappears and orthochlorobenzophenone separates; on heating with an alcoholic solution of hydrogen sulphide, it gives a mixture of chlorobenzophenone and chlorothiobenzophenone.

Orthomethylbenzophenonephenylimine melts at 104·5°, and crystallises from alcohol in stout, yellow needles. T. M. L.

Decomposition of Homologues of Benzophenone by Halogen Acids. By MAX WEILER (*Ber.*, 1899, **32**, 1908—1911).—When mesitoylmesitylene, C₆H₂Me₃·CO·C₆H₃Me₂ [2 : 4 : 6 : 3′ : 5′], is heated for 8 hours with concentrated hydriodic acid and phosphorus at 160—180°, it is decomposed to the extent of 50 per cent. into mesitylene and mesitylenic acid, a small proportion only of *pentamethyldiphenylmethane* being obtained in the form of flat needles melting at 67—68°. This fact is of interest since benzophenone (Graebe, Abstr., 1875, 457), meta- and paramethylbenzophenone, diparatolylketone (Ador and Rilliet, *Ber.*, 1879, 2298), parethylbenzophenone, and 4-benzoylmetaxylene (Söllscher, Abstr., 1882, 1292) yield only the

corresponding diphenylmethanes on treatment with hydriodic acid. Concentrated hydrochloric acid at 150—160° hydrolyses mesitoylmesitylene to the extent of 15 per cent., and benzoylmesitylene to the extent of 40 per cent., at 190°; moreover, the latter yields 62 per cent. of the benzoic acid and mesitylene required by theory when heated with concentrated hydrobromic acid of sp. gr. 1·49 for 18 hours at 190°. No hydrolysis, however, occurs when the compounds mentioned are boiled with alcoholic soda or with sodium dissolved in amylic alcohol; they are easily reduced, however, to the corresponding hydrols by zinc dust and dilute alcoholic potash, and these are then easily converted into the corresponding diphenylmethanes by reduction with hydriodic acid in presence of phosphorus.

The author summarises his results and those of a similar nature obtained by others (Louïse, *Ann. Chim. Phys.*, 1885, [vi], **6**, 206; Elbs, Abstr., 1887, 940; Victor Meyer, Abstr., 1895, i, 466, and Muhr, *ibid.*, i, 231) in the generalisation that orthomethylbenzophenones are easily hydrolysed by acids to the corresponding orthomethylated hydrocarbon and the carboxylic acid of the other radicle; thus the action $ArMe \cdot CO \cdot Ar + H_2O = ArHMe + Ar \cdot COOH$ takes place, although that expressed by the equation $ArMe \cdot CO \cdot Ar + H_2O = ArMe \cdot COOH + ArH$, never occurs.

Mesitoyl chloride (Fittig and Brückner, *Annalen*, 1868, **147**, 47), when pure, is a strongly refracting oil, which boils at 109·5° under 10 mm. pressure; *mesitoylmesitylene (dimesityl ketone)*, $C_{18}H_{20}O$, prepared by the action of aluminium chloride on a solution of mesitylene and mesitoyl chloride in carbon bisulphide, crystallises from alcohol in colourless, stellar aggregates of prisms, and melts at 84—85°. W. A. D.

The Six Isomeric Monohydroxybenzylideneacetophenones. (Monohydroxychalkones). By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1899, **32**, 1921—1926).—It is proposed to apply the name *chalkone* to benzylideneacetophenone,

$$\langle \, \rangle —CO \cdot CH : CH— \langle \, \rangle .$$
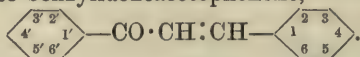
The properties of the six hydroxychalkones are shown in the following table:

|	Crystals.	M. p.	Solution in alkali.	Solution in H_2SO_4.	M. p. of acetyl derivative
2′-Hydroxychalkone	Yellow needles.	88—89°	Orange	Yellow	51—52°
3′-*Hydroxychalkone*.	Pale-yellow tablets.	126	Yellow	Yellow-ish-red	101
4′-*Hydroxychalkone*.	Yellow needles.	172—173	,,	,,	90
2-Hydroxychalkone	Yellow flakes.	153—155	Yellow-ish-red	,,	68— 69
3-Hydroxychalkone	White flakes.	159—160	Pale yellow	Yellow	102—103
4-Hydroxychalkone	Pale-yellow scales.	182—183	Deep yellow	Orange	129—131

It will be seen that the orthohydroxy-compounds are more intensely coloured than the para-compounds, and that the meta-compounds are less strongly coloured. The influence of the hydroxyl group is more pronounced in the aldehyde residue than in the ketone residue. The metahydroxy-compounds have been shown to have the lightest colour in the case of the three monohydroxybenzylideneindanediones, $C_6H_4{<}^{CO}_{CO}{>}C{:}CH \cdot C_6H_4 \cdot OH$, and the three monohydroxybenzylidene-bromindanones, $C_6H_3Br{<}^{CH_2}_{CO}{>}C{:}CH \cdot C_6H_4 \cdot OH$, but in the case of the hydroxyxanthones and the three nitrophenols the metahydroxy-compounds have an intermediate tint (Abstr., 1898, 32, 271; 1893, i, 217). T. M. L.

2 : 4'-Dihydroxyflavone. By STANISLAUS VON KOSTANECKI and S. ODERFELD (*Ber.*, 1899, **32**, 1926—1930. Compare this vol., i, 370).—
2' : 5'-*Diethoxy*-4-*methoxychalkone*, $C_6H_3(OEt)_2 \cdot CO \cdot CH{:}CH \cdot C_6H_4 \cdot OMe$, prepared from 2 : 5-diethoxyacetophenone and anisaldehyde, crystallises from alcohol in yellow needles, melts at 76·5—77·5°, and is coloured dark-red by concentrated sulphuric acid, giving a yellowish-red solution. 2-*Ethoxy*-4'-*methoxyflavanone*, $OEt \cdot C_6H_3{<}^{O-CH \cdot C_6H_4 \cdot OMe}_{CO \cdot CH_2}$, from 2-hydroxy-5-ethoxyacetophenone and anisaldehyde, crystallises from alcohol in long, colourless needles and melts at 131—132°; it dissolves in alcohol with a blue fluorescence, in concentrated sulphuric acid with a yellowish-red colour, and in alcoholic potash to a red solution from which water precipitates the original compound. The *monobromo*-compound crystallises from alcohol in white needles and melts at 140—141°. 2-*Ethoxy*-4'-*methoxyflavone*,

$$OEt \cdot C_6H_3{<}^{O-C \cdot C_6H_4 \cdot OMe}_{CO \cdot CH},$$
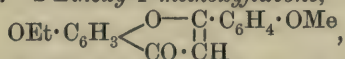
crystallises from dilute alcohol in very pale, yellowish, mono-hydrated needles; the yellow tint is probably due to impurities, since diethoxyflavone is colourless; the anhydrous substance melts at 134—135°, and dissolves in concentrated sulphuric acid to a pale yellow solution with a green fluorescence; sodium ethoxide decomposes it into 2-hydroxy-4-ethoxyacetophenone and anisic acid. By heating with concentrated hydriodic acid, it is converted into 2 : 4'-*dihydroxyflavone*, which crystallises from alcohol in slender, colourless needles, and chars at 320° without melting; concentrated sulphuric acid colours the crystals yellow, and gives a pale yellow solution with a slight green fluorescence; it dissolves in caustic soda to a greenish-yellow solution. The *diacetate* crystallises from a mixture of alcohol and acetic acid in white needles, and melts at 207°. 2 : 4'-*Diethoxyflavone* crystallises from alcohol in pure white needles and melts at 143°; concentrated sulphuric acid colours the crystals yellow, and gives a pale yellow solution with a fine green fluorescence.

T. M. L.

Oxime and Phenylhydrazone of Xanthone. By CARL GRAEBE and PAUL RÖDER (*Ber.*, 1899, **32**, 1688—1690).—*Xanthonephenylimine*,

$O{<}{C_6H_4 \atop C_6H_4}{>}C{:}NPh$, separates from alcohol in golden-yellow crystals and melts at $134\cdot5°$; it dissolves in concentrated sulphuric acid with a yellow colour and a green fluorescence, dissolves in concentrated hydrochloric acid, and gives a deep yellow *hydrochloride* which is decomposed by boiling water into xanthone and aniline, does not dissolve in alkalis, and is reduced to xanthen by heating with zinc dust. By boiling with an alcoholic solution of hydrogen sulphide it is converted into *xanthione*, $O{<}{C_6H_4 \atop C_6H_4}{>}CS$, isomeric with Graebe and Schulthess' thioxanthone, $S{<}{C_6H_4 \atop C_6H_4}{>}CO$; this melts at $156°$ and crystallises in long, dichroic needles which appear either dark red or brownish-red; it is yellow by transmitted light, and is also precipitated as a yellow powder on adding water to an alcoholic solution; the alcoholic solution is green, but, by reason of a strong fluorescence, appears red, or reddish-brown; it is very readily soluble in carbon bisulphide, and gives an intensely green solution with but slight fluorescence; concentrated sulphuric acid dissolves it to a yellow solution with a green fluorescence. *Xanthoneoxime*, $O{<}{C_6H_4 \atop C_6H_4}{>}C{:}NOH$, prepared by the action of hydroxylamine on xanthione, forms colourless crystals, melts at $161°$, and dissolves in concentrated sulphuric acid to a yellow solution with a blue fluorescence; it dissolves in hydrochloric acid, but is reprecipitated by water, and on boiling the solution xanthone is formed; it dissolves only with difficulty in caustic alkalis. *Xanthonephenylhydrazone*, $O{<}{C_6H_4 \atop C_6H_4}{>}C{:}N{\cdot}NHPh$, prepared by the action of phenylhydrazine on xanthione, crystallises from alcohol in golden-yellow needles and melts at $152°$; it dissolves in concentrated sulphuric acid to a yellow solution with a green fluorescence; concentrated hydrochloric acid converts it into an orange-yellow *hydrochloride*, which dissolves on warming to an orange-yellow solution; on boiling the solution, it is decomposed and xanthone separates in colourless or yellowish needles. T. M. L.

Hydroxylamine Derivatives of Tetrahydropyrone Compounds. By PAWEL IW. PETRENKO-KRITSCHENKO and S. ROSENZWEIG (*Ber.*, 1899, **32**, 1744—1748).—The *oxime* of orthodiethoxydiphenyltetrahydropyrone, $O{<}{CH(C_6H_4{\cdot}OEt){\cdot}CH_2 \atop CH(C_6H_4{\cdot}OEt){\cdot}CH_2}{>}C{:}NOH$ (this vol., i, 440), melts at $133°$; it crystallises with 1 mol. of ethylic alcohol, acetic acid, pyridine, methylic alcohol, acetone, or chloroform; the first three compounds have an indeterminate melting point at $109°$, $109°$, and $85°$ respectively; in all cases the molecule of solvent is expelled readily by drying (at $100°$?). When a solution of the oxime in chloroform, acetic acid, or acetone is saturated with hydrogen chloride and allowed to crystallise, the *hydrochloride* of the oxime is obtained; this melts and decomposes at $154°$.

The *oximes* of orthodimethoxydiphenyltetrahydropyrone (*loc. cit.*)

and diphenyltetrahydropyrone (this vol., 1897, i, 142), which melt at 202° and 154°, yield additive products in the same way.

These oximes are obtained quite readily; on the other hand, tetrahydropyrones in which an H of each CH_2 group has been replaced, for example, by COOEt, do not yield oximes. C. F. B.

Constitution of Phenolphthalein. By HANS MEYER (*Monatsh.*, 1899, **20**, 337—368).—When phenolphthalein oxime, suspended in alcohol, is heated with a concentrated aqueous solution of hydroxylamine hydrochloride, parahydroxyphthalanil, $C_6H_4[C(NOH)\cdot C_6H_4\cdot OH]_2$, identical with Piutti's compound (Abstr., 1886, 1026), is formed; it crystallises in small, colourless scales with a silvery lustre, melts at 292° (Piutti gave 287°), is easily soluble in boiling alcohol, soluble in ether or ethylic acetate, and insoluble in water. Its solutions in fixed alkalis are yellow; its solution in ammonia is colourless, but becomes violet when exposed to the air, probably owing to partial conversion into phthalimide and amidophenol, for the latter compound gives the same reaction. The acetyl derivative of parahydroxyphthalanil melts at 237°. By the action of dilute hydrochloric or sulphuric acid, parahydroxyphthalanil is decomposed into phthalic acid and amidophenol. Since hydroxybenzoylbenzoic acid does not react with hydroxylamine hydrochloride in alkaline or neutral solution, the formation of hydroxyphthalanil must be due to the intermediate production of the dioxime of phenolphthalein.

Parahydroxyphenylphthalazone, $C_6H_4\!\!<\!\!{}^{C(C_6H_4\cdot OH)}_{CO}\!\!{}^{>}_{NPh}\!\!>\!N$, is formed, together with amidophenol, by gently warming phenolphthaleinmonoxime with phenylhydrazine, acetic acid, and alcohol or water for a short time, and is also obtained by the action of phenylhydrazine on hydroxybenzoylbenzoic acid; it forms small, colourless needles which gradually become yellow or green when exposed to the light, melts at 272°, is easily soluble in boiling alcohol, sparingly so in alkalis, insoluble in water or acids, and forms a yellow solution in concentrated sulphuric acid.

By the action of aqueous or alcoholic ammonia on phenolphthalein at the ordinary temperature, iminophenolphthalein (Errera and Gasparini, Abstr., 1894, i, 294) is formed, together with a small quantity of gummy or amorphous substances which contain nitrogen.

When an alcoholic solution of orthohydroxybenzoylbenzoic acid is reduced with zinc and hydrochloric acid, Bistrzycki and Oehlert's hydroxyphenylphthalide (Abstr., 1897, i, 600) is obtained; it melts at 157—160°, not at 148—151°, and by melting a mixture of this substance with paramidophenol, a compound melting at 252—256°, and identical with that prepared by reducing phenolphthalein itself, is formed. Hence phenolphthalein in coloured alkaline solutions has a symmetrical constitution, $C_6H_4(CO\cdot C_6H_4\cdot OK)_2$, whilst in neutral or colourless alkaline solutions it reacts as a lactone, $CO\!\!<\!\!{}^{C_6H_4}_{O}\!\!>\!C(C_6H_4\cdot OH)_2$.

The change from the lactone to the diketone form corresponds with that of unsaturated phthalides into diketohydrindene derivatives, and the reverse change resembles the intramolecular rearrangement of

benzilic acid. The phthaleins which are insoluble in alkalis are also converted into the coloured, symmetrically constituted, forms by the action of concentrated acids.

Diphthalylic acid forms two diethylic salts, a coloured and a colourless one, and there are two modifications of benzilcarboxylic acid, of which one is colourless and the other yellow. 　　　　　E. W. W.

Acetylation of α-Naphthylamine. By EUGEN BAMBERGER (*Ber.*, 1899, **32**, 1803—1804. Compare Gattermann, this vol., i, 516). —In the preparation of acetyl-α-naphthylamine by Gattermann's method, a considerable quantity (in some cases over 50 per cent. of the base employed) of the *diacetyl* derivative, $C_{10}H_7NAc_2$, is always formed; it is characterised by the readiness with which it crystallises, yielding clear, rhombic prisms melting at 128—129°, and soluble in light petroleum or alcohol. β-Naphthylamine and aniline also yield diacetyl derivatives when heated with acetic anhydride, but only in small quantities. 　　　　　　　　　　　　　　　J. J. S.

Isomeric Naphthalene Derivatives. By PAUL FRIEDLÄNDER, H. HEILPERN, and M. SPIELFOGEL (*Chem. Centr.*, 1899, i, 288—289; from *Mitt. Technol. Gewerb.-Mus., Wien*, [ii], **8**, 316—323).—1 : 2-Nitronaphthylamine is best prepared by adding concentrated nitric acid to β-acetonaphthalide suspended in ice-cold glacial acetic acid; the 1 : 2-nitracetonaphthalide formed is extracted with benzene and then hydrolysed by boiling with alcoholic potash. 1 : 2-Nitronaphthylamine may also be obtained by the action of concentrated nitric acid on β-naphthyloxamic acid below 40°. *β-Naphthyloxamic acid*, prepared by heating β-naphthylamine with oxalic acid at 140—150°, crystallises from glacial acetic acid in white leaflets, melts at 190°, is slightly soluble in water, readily in alcohol or ether, and forms easily soluble sodium and ammonium salts and sparingly soluble calcium and barium salts. 1 : 2-*Nitronaphthonitrile*, prepared by diazotising 1 : 2-nitronaphthylamine in alkaline solution and then treating with potassium cuprous cyanide, crystallises in light brown needles, melts at 101°, and is easily soluble in alcohol, benzene, or glacial acetic acid. 4 : 2-*Nitronaphthoic acid*, obtained by boiling 1 : 2-nitronaphthonitrile with baryta water for a long time, crystallises from chloroform in reddish needles, melts at 182°, and forms alkali salts which are easily soluble in water.

4′ : 2-*Nitronaphthonitrile* is prepared from 4′ : 2-nitronaphthylamine; it crystallises from 25 per cent. acetic acid solution in yellowish-brown, and from alcohol in copper-red, needles, melts at 168°, and by the action of dilute sulphuric acid at 150° forms 4′ : 2-*nitronaphthamide*, which crystallises from acetone in brownish-yellow needles and melts at 261—263°. The corresponding 4′ : 2-*nitronaphthoic acid* crystallises from alcohol in yellowish-white needles, melts at 286—287°, and is slightly soluble in alcohol, very slightly so in water, and easily in acetone; the ammonium, sodium, and barium salts crystallise in needles, the two former being easily, but the last only very slightly, soluble in water. This acid appears to be identical with that obtained by nitrating β-cyanonaphthalene. 1′ : 2-*Nitronaphthonitrile*, prepared from the corresponding amine, crystallises from benzene and alcohol in needles, and melts at 143°. 1′ : 2-*Nitronaphthamide* crystallises from

alcohol in brownish-yellow needles and melts at 218°. 1′:2-*Nitronaphthoic acid* crystallises from alcohol in pale brown needles and melts at 295°.

1 : 4′-*Amidonaphthonitrile*, obtained by distilling a mixture of sodium naphthylaminesulphonate with potassium ferrocyanide, crystallises from acetic acid in greenish-yellow needles, melts at 137°, is slightly soluble in hot water, alcohol, or ether, and when hydrolysed with sulphuric acid (2 : 1) yields 1 : 4′-amidonaphthoic acid. 1 : 4′-*Hydroxynaphthoic acid*, prepared by treating a solution of 1 : 4′-amidonaphthoic acid with a diazotised solution of paranitraniline and boiling with a small quantity of carbamide, crystallises in small, white needles, melts at 219°, is easily soluble in acetic acid, alcohol, or ether, slightly so in water, and forms an insoluble copper salt. *Ethylic* 1 : 4′-*hydroxynaphthoate* crystallises from a mixture of benzene and light petroleum in small, white needles, melts at 73°, is easily soluble in alcohol, ether, or benzene, slightly so in light petroleum, and insoluble in water. 2 : 2′-*Amidonaphthonitrile* crystallises from toluene in pale yellow needles and melts at 170—171°. 2 : 2′-*Amidonaphthoic acid* crystallises in white needles and melts at 245°. 2 : 2′-*Hydroxynaphthoic acid* crystallises in leaflets and melts at 245°. 1 : 2′-*Amidonaphthonitrile* melts at 117°. E. W. W.

Isomeric Naphthalene Derivatives. By PAUL FRIEDLÄNDER and ARMIN FISCHER (*Chem. Centr.*, 1899, i, 289; from *Mitt. Technol. Gewerb.-Mus., Wien*, [ii], **8**, 324—325).—Sodium hydrogen β-nitronaphthalenedisulphonate is prepared by adding 10 parts of a mixture of equal parts of nitric and sulphuric acids to 28 parts of powdered 1 : 4′-naphthalenedisulphonic acid suspended in 90 parts of sulphuric acid, the mixture being well cooled. The product, after remaining a short time, is poured on to ice and treated with 40 parts of sodium carbonate. *Sodium β-naphthylaminedisulphonate*, prepared by reducing the corresponding nitro-salt (German Patent, 65997), crystallises in broad, white needles, is easily soluble in hot water, very slightly in absolute alcohol, and may be salted out of its aqueous solution by means of sodium chloride; the alkaline solution has a bluish-violet fluorescence. The *acid barium* salt, $[HSO_3 \cdot C_{10}H_5(NH_2) \cdot SO_3]_2Ba$, prepared by boiling the solution of the sodium salt with a concentrated solution of barium chloride for a long time, crystallises in very small needles, and is slightly soluble in water. *β-Naphthylaminedisulphonic acid*, $NH_2 \cdot C_{10}H_5(SO_3H)_2$ $[SO_3H : NH_2 : SO_3H = 1′ : 2 : 4]$, obtained by decomposing the barium salt with dilute sulphuric acid, crystallises in concentrically grouped prisms, and is slightly soluble in moderately concentrated sulphuric acid. E. W. W.

Terpenes and Ethereal Oils. Pinole. By OTTO WALLACH [WILHELM STIEHL, ADOLF SIEVERTS and R. SIEVERTS], *Annalen*, 1899, **306**, 267—282. Compare Abstr., 1896, i, 571).—Although the constitution of pinole is well represented by the formula already given (Abstr., 1896, i, 101), certain anomalies present themselves in the behaviour of pinole tribromide, obtained by adding the elements of hydrogen bromide to pinole dibromide.

Isopinole dibromide, $C_{10}H_{16}Br_2O$, produced on eliminating hydrogen

bromide from pinole tribromide by means of quinoline in benzene, or of silver acetate in ethylic acetate, separates from ether in transparent, well-formed crystals, which differ in habit from the isomeride, but melt at 94°; it is noteworthy that the substance is unsaturated, yielding pinole tribromide with hydrogen bromide, and with bromine the *tetrabromide*, $C_{10}H_{16}Br_4O$, which melts at 132°. When a solution of pinole tribromide in glacial acetic acid is digested with silver acetate, the *compound* $C_{12}H_{20}Br_2O_3$ is produced; it crystallises from methylic alcohol and melts at 118—120°.

Hot 10 per cent. potassium hydroxide converts pinole tribromide and isopinole dibromide into inactive carvone, but sodium methoxide gives rise to the methylic ether of carveol or carvacrol.

Pinolone, $C_{10}H_{16}O$, obtained by reducing isopinole dibromide in glacial acetic acid with zinc dust, has the odour of amylic acetate, boils at 214—217°, and has a sp. gr. 0·916 and refractive index n_D 1·46603 at 20°. The *semicarbazone* melts at 158°, and the *oxime* boils at 150° under 15 mm. pressure; reduction of the latter converts it into a base, the *carbamide* derivative of which crystallises from methylic alcohol, and melts at 186°.

Pinolol, $C_{10}H_{17}\cdot OH$, prepared from the ketone by reduction in alcohol with sodium, has the odour of linalool, boils at 108° under 15 mm. pressure, and has a sp. gr. 0·913, and refractive index n_D 1·47292 at 20°.

The derivative of pinole with nitrosyl chloride melts at 116—120° when rapidly heated, and is very sparingly soluble in methylic alcohol; the solution in chloroform is colourless at $-12°$, becoming blue as the temperature rises. The compound in question is pinole *bisnitrosochloride*, which is colourless in the dimolecular form, becoming blue on dissociation.

Pinole *isonitrosochloride*, prepared by passing hydrogen chloride into a solution of the bisnitrosochloride in ethylic acetate, is also produced by the slow, spontaneous change of the dimolecular compound; it dissolves in methylic alcohol, crystallises from ethylic acetate in colourless, transparent prisms, and melts at 131°, becoming brown and evolving gas at 150°; the compounds which it yields with bases are identical with those derived from the dimolecular compound.

When the bisnitrosochloride or the isonitrosochloride is heated with an alcohol, chlorine is replaced by hydroxyl. Methylic alcohol yields the *compound* $OMe\cdot C_{10}H_{15}:NOH$, which crystallises in needles and melts at 138°; the *compound* $OEt\cdot C_{10}H_{15}:NOH$, obtained by the action of ethylic alcohol, forms prisms melting at 100°.   M. O. F.

Oil of Lemon-Grass. By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], **21**, 77—79).—This essence is mixed with sodium hydrogen sulphite solution, and the crystals of the bisulphite compound obtained are dissolved in water and mixed with barium chloride solution; the barium salt of the citronellal compound is precipitated and the aldehyde regenerated by the action of alcoholic potash; the filtrate from the insoluble citronellal compound is treated with aqueous potash in order to regenerate the citral. The original oil contains 76—77 per cent. of citral, and 7—8 per cent. of citronellal, besides small

quantities of geraniol and methylheptenone (compare Tiemann, Abstr., 1898, i, 677).　　　　　　　　　　　　　　　　　　　　　　G. T. M.

Essential Oils of Lemon-Grass and Citronella. By JULIEN FLATAU (*Bull. Soc. Chim.*, 1899, [iii], **21**, 158—159).—Ziegler's conclusion that the formation of several isomeric semicarbazones proves the existence of various isomerides of citral in oil of lemon-grass is untenable, since carefully purified citral obtained from geraniol yields a mixture of semicarbazones having melting points ranging from 140° to 155°. Oil of lemon-grass consists chiefly of citral, but small quantities of methylheptenone and 2—4 per cent. of citronellal are also present. Oil of citronella contains 25—30 per cent. of citronellal and 2—5 per cent. of citral.　　　　　　　　　　　　　　N. L.

Ethereal Salts in Oil of Lemon-Grass. By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], **21**, 159—160).—The high boiling residue previously obtained in the examination of oil of lemon-grass is now shown to consist principally of the ethereal salts of a terpenic alcohol, probably geraniol, with capric and caproic acids which were identified and separated by means of their barium salts.　　　　　　　N. L.

The Three Aldehydes of Oil of Lemon-Grass. By WILHELM STIEHL (*J. pr. Chem.*, 1899, [ii], **59**, 497—516).—The author attributes the differences between his results (this vol., i, 66) and those of Tiemann (*ibid.*, i, 247 and 623) partly to impurities in the latter's material. He upholds the existence of these three aldehydes and attempts to explain their isomerism on stereochemical grounds.
　　　　　　　　　　　　　　　　　　　　　　R. H. P.

Isomeric Aldehydes from ¡Oil of Lemon-grass. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1899, [iii], **21**, 419—423).—Of the three isomeric semicarbazones prepared by Barbier and the author from oil of lemon-grass (Abstr., 1896, i, 311), that melting at 135° proves to be a mixture of the other two melting at 171° and 164° respectively. These two semicarbazones correspond with Tiemann's citral *a* and citral *b* (this vol., i, 249).　　　　　　　T. H. P.

Constituents of Oil of Petit Grain. By EUGÈNE CHARABOT and LOUIS PILLET (*Bull. Soc. Chim.*, 1899, [iii], **21**, 74—75. Compare this vol., i, 620).—The essence obtained from the leaves and young shoots of *Citrus bigaradia* is hydrolysed and fractionated. The portion distilling below 185° contains no appreciable amount of limonene if care has been taken to exclude the fruit from the raw material. The portion distilling below 197° contains linalool, and this substance forms the chief constituent of the fraction 197—200°; it is separated from geraniol by means of phthalic anhydride and identified by its optical properties and by oxidation to citral. The fraction 220—232° consists chiefly of geraniol which is isolated by means of calcium chloride. The fraction 200—220° contains a mixture of the two alcohols. The hydrolysed oil contains approximately 70—75 per cent. of linalool and 10—15 per cent. of geraniol. The liquid portion of the residue, after distillation, gives the reactions of sesquiterpenes.　　　　G. T. M.

Empyreaumatic Oil of Juniper. By CATHELINEAU and JEAN HAUSSER (*Bull. Soc. Chim.*, 1899, [iii], **21**, 378—380).—The fraction

extracted by amylic alcohol from that portion of empyreaumatic oil of juniper which is soluble in 5 per cent. aqueous soda (this vol., i, 536) is separated by treatment with hot water into an insoluble, resinous substance, which constitutes from one-third to one-sixth of the whole fraction, and a feebly alkaline solution. The former portion becomes semi-fluid when heated, and is readily soluble in alcohol, chloroform, amylic alcohol, or concentrated acetic acid, but only partially soluble in ether. It is precipitated from its alcoholic solution by normal lead acetate and reduces ammoniacal silver nitrate solution, but has no action on Fehling's solution. Fusion with potash decomposes it into an insoluble resin and a soluble, alkaline portion in which small quantities of resorcinol and pyrogallol were detected.

The alkaline, aqueous solution obtained from the amylic alcohol extract yields, when acidified, a semi-fluid precipitate which is very soluble in alcohol, insoluble in water, ether, or light petroleum. It is precipitated from alcoholic solution by normal lead acetate, reduces ammoniacal silver nitrate solution, but has no action on Fehling's solution. On exposure to air, or on heating with a small quantity of sulphuric acid, it absorbs oxygen and becomes resinous. It is decomposed by heat under ordinary conditions, but by cautious distillation under diminished pressure a phenolic substance was obtained, having an odour of creosote and boiling at 215—250° at the ordinary pressure.

From these results, it is concluded that the amylic alcohol extract of the oil consists ·for the most part of phenolic ethers of resinous compounds.   N. L.

Tuberone, the Aromatic Principle of the Tuberose Flower. By ALBERT VERLEY (*Bull. Soc. Chim.*, 1899, [iii], 21, 306—309).— By distilling in a vacuum a concentrated extract of tuberose, a small quantity of a pure product, boiling at 167° under 15 mm. pressure, is obtained. This substance, which the author calls *tuberone*, possesses in a high degree the odour of the tuberose, which slightly resembles that of coumarin, but is much more fragrant and persistent. It has a sp. gr. 0·9707 at 8°, and a refractive index n_D 1·516 at 14°; it has the formula $C_{13}H_{20}O$, which is the same as that of irone obtained from the root of the iris, and is an unsaturated compound, as it decolorises aqueous permanganate, whilst its behaviour with bromine shows that the molecule contains one double linking; probably the constitution may be expressed by the formula, $\begin{array}{l} CH_2 \cdot CH_2 \cdot CH \cdot CO \cdot CH_2 \\ CH_2 \cdot CH_2 \cdot CH \cdot CH_2 \cdot CH \cdot CH_2 \cdot CH:CH_2 \end{array}$
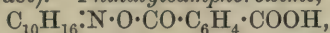
Acetic anhydride has no action on tuberone even on boiling for several hours, but heating with phenylhydrazine causes the elimination of water, indicating the presence of a carbonyl group in the molecule. On heating tuberone with aqueous chromic acid in a reflux apparatus, formaldehyde is produced together with an oily acid which, however, was obtained in quantity insufficient for analysis.   T. H. P.

Derivatives of Camphoroxime. By GEORGE B. FRANKFORTER and A. D. MAYO (*Amer. Chem. J.*, 1899, 21, 471—473).—The action of acid chlorides and anhydrides on camphoroxime usually leads

to loss of water and formation of campholenic nitrile, but under certain conditions ethereal salts are formed. *Acetylcamphoroxime,* $C_{10}H_{16}$:NOAc, prepared by the action of acetic anhydride on camphoroxime in the cold, is a colourless oil of aromatic odour, and boils and decomposes at 170°; it is insoluble in water, but is slowly hydrolysed by it, and is rapidly hydrolysed by sodium hydroxide.

Chloralcamphoroxime, $CCl_3 \cdot CH(\cdot ON:C_{10}H_{16})_2 + 2H_2O$, prepared by the action of chloral on camphoroxime in cold ethereal solution, separates from alcohol as a fine, white, crystalline, powder, melts at 82°, dissolves in ether or alcohol but not in water, and very readily decomposes. *Succinylcamphoroxime,* $C_{10}H_{16}$:NO·CO·$CH_2 \cdot CH_2 \cdot COOH$, prepared by boiling camphoroxime with succinic anhydride in ethereal solution, is a colourless oil boiling and decomposing at 246°, and is hydrolysed by alkalis or by boiling with water. T. M. L.

Derivatives of Camphoroxime. By GEORGE B. FRANKFORTER and P. M. GLASOE (*Amer. Chem. J.*, 1899, 21, 474—478. Compare preceding abstract).—*Phthalylcamphoroxime,*
$$C_{10}H_{16}:N \cdot O \cdot CO \cdot C_6H_4 \cdot COOH,$$
prepared by boiling a solution of camphoroxime in benzene or toluene with an excess of phthalic anhydride, melts at 135·5° with decomposition into phthalic acid and campholenic nitrile, and dissolves in ether, alcohol, chloroform, or benzene, but not in carbon bisulphide; it crystallises from dilute alcohol in fine, white needles, but on boiling an alcoholic solution it decomposes slowly into campholenic nitrile and phthalic acid, together with a small quantity of a colourless, odourless oil, which is, perhaps, an ethylic salt of phthalyloxime; it is readily hydrolysed by caustic soda.

Camphorformaldoxime, $C_{10}H_{16}$:N·O·$CH_2OH + H_2O$, separates in large, white crystals when camphoroxime is heated on a water-bath with formaldehyde and the resulting oil is left covered with water; it melts at 62—63°, and can be recrystallised from water, but by strong acids or by boiling the aqueous solution is decomposed into camphoroxime and formaldehyde.

Camphorparaformaldoxime, $C_{10}H_{16}$:N($C_3H_5O_3$), separates as a thick oil when camphoroxime is heated with an excess of formaldehyde and allowed to remain in a warm place in direct sunlight; when dropped into water containing a little formaldehyde, it passes into the preceding compound.

Chlorocamphoroxime, $C_{10}H_{15}Cl$:NOH, separates quantitatively in fine needles on adding an ethereal solution of sulphuryl chloride to an ethereal solution of camphoroxime, and melts at 290°; the position of the chlorine atom has not yet been ascertained. T. M. L.

Opopanax from Umbelliferæ. By ALEXANDER TSCHIRCH and A. KNITL (*Arch. Pharm.*, 1899, 237, 256—270).—The sample of opopanax examined was the product of the *Opopanax Chironium*, Koch (*Ferula Opopanax*, L.; *Laserpitium Chironium*, L.; *Pastinaca Opop., O. orient.*, Boiss). It was extracted with alcohol, when a gum remained undissolved. By extracting the alcoholic solution, which contained resin, with light petroleum, an essential oil was obtained. After

evaporation of the alcohol, the resin which remained was dissolved in ether ; a small portion, possessing the character of a tannol, remained undissolved. By shaking the ethereal solution with a concentrated solution of sodium hydrogen sulphite, vanillin was extracted. By shaking the ethereal solution next with 2—5 per cent. sodium carbonate solution until the former was no longer acid in reaction, ferulic acid was obtained. By boiling the resin with potassium carbonate solution 8 hours a day for 4 months, or by hydrolysing it with sulphuric acid instead, ferulic acid was obtained, but the loss in purification was very great. The alcohol produced simultaneously, *oporesinotannol*, was puri-fied by dissolving it 40 times in alcohol and precipitating it with water acidified with hydrochloric acid, and then digesting it with light petr-oleum. It is a light brown powder, and has the character of a resino-tannol and the composition $C_{12}H_{13}O_2 \cdot OH$. It yields a light brown *mono-benzoic* derivative when treated by the Schotten-Baumann method, but no acetyl derivative could be obtained. With bromine, it yields a sub-stitution derivative; strong nitric acid converts it on the water-bath into picric and oxalic acids. When dry-distilled, it yields no umbelliferone.

A list of the resinotannols hitherto discovered is given, with their composition, acetyl and benzoyl derivatives, and the products of their oxidation with nitric acid and fusion with potash.

The gum was purified by repeated precipitation with alcohol; it contained 3·53 per cent. of ash, of which 1·67 was calcium and 0·19 magnesium. An arabic acid was prepared from it by dissolving it 40 times in water acidified with hydrochloric acid and precipitating it with alcohol ; this contained C 43·17, H 6·42 per cent., a composition which lies between $C_{12}H_{22}O_{11}$ and $C_6H_{10}O_5$. When oxidised with dilute nitric acid on the water-bath, it yields an acid apparently identical with mucic acid. Neither the acid nor the crude gum is optically active. A list is given of the various arabic acids hitherto obtained, with their sources and composition.

By dissolving the essential oil in ether, shaking the mixture with a solution of sodium hydrogen sulphite, and treating the solution with ether, a waxy product was obtained, which, on sublimation, yielded needles which melted at 133—134°, and had the composition C 66·6, H 2·7 per cent. ; this substance is named *oponal*.

The resin also contained small quantities of a bitter substance, but this could not be obtained in crystals.

The drug contained, in 100 parts : Resin soluble in ether (oporesino-tannol ferulate) 51·8, resin insoluble in ether (free oporesinotannol), 1·90, gum 33·8, essential oil 8·3, free ferulic acid 0·22, vanillin 0·0027, moisture 2·0, bassorin and plant remains 2·0.

The authors have been unable to prepare from galbanum resin the galbanic acid described by Hirschsohn (*Chem. Zeit.*, 1893, 195). A sample of Hirschsohn's acid yielded, on sublimation, crystals which melted at 157—158°, and had the composition $C_{40}H_{60}O_4$; they seem to be identical with, or closely related to, the lævopimaric acid of galipot.

Umbelliferone has been obtained from Sumbul root, but not from *Rad. levistici* or *Mei.* C, F, B,

Cinnamein or Oil of Peru Balsam. By HERMANN THOMS (*Arch. Pharm.*, 1899, **237**, 271—284).—An undoubtedly genuine specimen of Peru balsam, collected personally by a traveller, was previously examined (*Ber. deut. pharm. Ges.*, 1898, 264), and specimens occurring in commerce are now found to have the same constituents. Vanillin can be extracted by shaking an ethereal solution of the balsam with a strong solution of sodium hydrogen sulphite. The ethereal solution can then be hydrolysed with alcoholic potash in the cold ; by distilling the product with steam, the alcohols can be driven over, and from the non-volatile residue a substance melting at about 80° and possessing the character of a phytosterol can be isolated. The acids set free on acidifying the residual alkaline solution with hydrochloric acid were shown to consist chiefly of a mixture of benzoic and cinnamic acids, the latter being present to the extent of nearly 40 per cent. The last mother liquors yielded a small quantity of an acid that melted at 79—80°, and appeared to be a *dihydrobenzoic acid*. The mixture of alcohols was fractionated under diminished pressure ; benzylic alcohol was obtained as the lower boiling fraction, and a new alcohol, *peruviol*, $C_{13}H_{22}O$, in much smaller amount, as a fraction boiling at 139—140° under 7 mm. pressure. This has a sp. gr. 0·886 at 17·5°, and a rotation $+13°$ in a 100 mm. tube ; it could not be made to yield an acetyl derivative in a pure state, but a *monocinnamoyl* derivative was obtained when it was heated with cinnamic chloride ; it takes up 4Br in acetic acid solution, and so is possibly a hydroaromatic compound with two double linkings in the side chains ; when it is oxidised with chromic acid in the cold, CH_2 appears to be replaced by O, which is an argument for the presence of a CH_2: group ; when oxidised with alkaline permanganate, at first in the cold, it yields acetic acid together with propionic or possibly butyric acid, and a small quantity of a crystalline acid not volatile with steam.

No iso- or allo-cinnamic acid, or any cinnamylic alcohol (styrone) could be detected in the balsam. C. F. B.

Composition of Vicin. By HEINRICH RITTHAUSEN (*J. pr. Chem.*, 1899, [ii], **59**, 480—481. Compare Abstr., 1881, 1158).—The empirical formula for vicin is $C_8H_{15}N_3O_6$, but as vicin yields sugar in appreciable quantity when warmed with dilute sulphuric acid, it is to be regarded as a glucoside, and the molecule must be some multiple of $(C_8H_{15}N_3O_6)$; the author was unable, however, to make a determination of the molecular weight. R. H. P.

Divicin. By HEINRICH RITTHAUSEN (*J. pr. Chem.*, 1899, [ii], **59**, 482—486. Compare Abstr., 1881, 1158).—Further analyses have been made of divicin, and the formula is now given as $C_4H_7N_4O_2$. An aqueous solution of divicin possesses strong reducing properties, and is oxidised by strong nitric acid (probably) to allantoin. R. H. P.

Composition of the Convicins obtained from the Seeds of Vetch and of Vicia Faba. By HEINRICH RITTHAUSEN and PREUSS (*J. pr. Chem.*, 1899, [ii], **59**, 487—488. Compare Abstr., 1881, 1158). —The convicins obtained from these sources proved to be completely identical. Convicin has the composition $C_{10}H_{15}N_3O_8 + H_2O$.

R. H. P.

Capsaicin. By KARL MICKO (*Chem. Centr.*, 1899, i, 293—294; from *Zeit. Unters. Nahr-Genussm.*, 1898, 818—829).—*Capsaicin*, $C_{18}H_{28}NO_3$, prepared from the ethereal extract of the fruit of *Capsicum annuum*, which yields 0·03 per cent., crystallises from light petroleum in transparent, colourless plates, melts at 63—63·5°, is easily soluble in ether, alcohol, chloroform, or benzene, rather less so in carbon bi-sulphide, very slightly in hot water, and insoluble in cold. The crystals easily fall into powder and the dust has an extremely irritating effect on the mucous membrane. An alkaline solution of capsaicin, containing only 0·01 gram in a litre, has a strong burning effect when placed on the tongue. When capsaicin is heated on platinum foil, it emits heavy, violently irritating fumes; it is not volatile in steam, and has the properties of a weak, phenol-like acid. When excess of platinic chloride is added to an alcoholic solution of capsaicin and the mixture allowed to evaporate, after a few hours it acquires the odour of vanillin; even small quantities of capsaicin give this reaction. The molecular weight determined by Beckmann's method in 0·5 per cent. benzene solution was found to be 316, and in 5 per cent. solution 643. The presence of a methoxy-group was proved by Zeisel's method and of a hydroxy-group by the Schotten-Baumann method. The *benzoyl* derivative, $OMe·C_{17}H_{24}NO·OBz$, prepared in alkaline solution, crystallises in silky needles and melts at 74°. The determinations of the molecular weight of this compound approached more nearly to the theoretical value.   E. W. W.

Compounds from Lichens. By WILHELM ZOPF (*Annalen*, 1899, 306, 282—321. Compare Abstr., 1895, i, 297; 1896, i, 103; 1897, i, 362, 436; 1898, i, 89, 489).—*Stictaurin*, the orange-red compound obtained from *Sticta aurata* (Ach.), is a derivative of pulvic acid, yielding calycin and ethylpulvic acid under the influence of boiling alcohol; the substance has been obtained from *Candelaria vitellina* (Ehrh.), *C. concolor* (Dicks.), and *Gyalolechia aurella* (Hoffm.), and is probably identical with dipulvic acid, obtained by Hesse from *Candelaria concolor*.

Caperatic acid, hitherto isolated by Hesse solely from *Parmelia caperata*, has been obtained by the author from *Platysma glaucum* (L.), and from *Mycoblastus sanguinarius* (L.).

Lichenostearic acid, which has been obtained only from Iceland moss (*Cetraria islandica*), occurs also in *Platysma cucullatum* (Bell.); the last-named lichen has yielded usnic acid, which is found also in *Pl. diffusum* (Nyl.), and in *Alectoria ochroleuca* (Ehrh.); the last-named contains barbatic acid.

Lecanoric acid occurs in *Psora ostreata*, Hoffm.; *Urceolaria cretacea*, Mass.; *Parmelia tiliacea* var. *scortea*, Ach.; *P. fuliginosa*, Fr., var. *ferrugin-ascens*, Zopf, and *P. verruculifera*, Nyl. With this compound has been identified parmelialic acid, previously described as occurring in *Urceolaria cretacea*, Mass., and in *Parmelia tiliacea* var. *scortea*, Ach.

Glomelliferin is a new compound obtained from *Parmelia glomellifera*, Nyl.; it crystallises from benzene in aggregates of slender needles and melts at 143—144°.

Atranoric acid has been already distinguished in forty-five lichens,

and also occurs in *Platysma glaucum* (L.), Nyl; *Mycoblastus sanguinarius* (L.), and *Parmelia omphalodes* (L.).

Lecidea sudetica contains salazinic acid.

Confluentin, which crystallises from hot benzene in aggregates of white prisms and melts at 147—148°, is obtained from *Lecidea confluens*, Fr.; *Platysma diffusum* (Web.) yields *diffusin*, which crystallises in silky needles and melts at 135—136°.

Stereocaulic acid occurs in *Stereocaulon pileatum*, Ach., and *Parmelia omphalodes* (L.). M. O. F.

Conversion of Unsaturated Ketoximes into Pyridine Derivatives. II. By MAX SCHOLTZ (*Ber.*, 1899, **32**, 1935—1939. Compare Abstr., 1895, i, 562).—*Methylcinnamylideneacetone*,

$$CHPh\dot{:}CMe\cdot CH\dot{:}CH\cdot COMe,$$
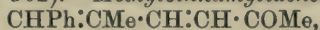
crystallises from alcohol in yellow needles, melts at 62°, and gives a blood-red coloration with concentrated sulphuric acid. The *oxime* crystallises from alcohol in needles, is almost white in colour, and melts at 128°. On dry distillation, it is converted into 2-*phenyl*-3 : 6-*dimethylpyridine*, a pale yellow oil boiling at 286—288° (corr.); the *platinochloride* crystallises in orange-yellow needles and melts at 220°; the *picrate* crystallises in yellow needles and melts at 179—180°.

Methylcinnamylideneacetophenone, $CHPh\dot{:}CMe\cdot CH\dot{:}CH\cdot COPh$, crystallises from hot alcohol in glistening, yellow flakes, melts at 81°, and gives a blood-red coloration with concentrated sulphuric acid. The *oxime* crystallises from hot alcohol in pale yellow needles and melts at 165°. On dry distillation, it gives 3-*methyl*-2 : 6-*diphenylpyridine* as a thick, yellow oil boiling at 253—255° under 25 mm. pressure; the *platinochloride* crystallises in orange-yellow needles; the *aurichloride* is precipitated as an oil, but the *mercurichloride*, $C_{18}H_{15}N,HCl,2HgCl_2$, crystallises in slender, white needles and melts at 160°. T. M. L.

Indigotinsubsulphonic Acids. By B. WILLIAM GERLAND (*J. Soc. Chem. Ind.*, 1899, **18**, 225—227).—When indigotin is heated at 100° for a few hours with sulphuric acid of sp. gr. 1·6—1·7, it is completely dissolved; the solution is, however, precipitated by water and the precipitate consists of a mixture of several subsulphonates with a varying amount of monosulphonate.

By carefully covering the surface of the acid solution with water and leaving it at rest for a few days, the author succeeded in getting the new substance in a crystalline state; it forms distinct but very fragile needles of a dark, almost black, colour. When the free acid has been removed by washing, it partially redissolves in water, and on adding to this solution calcium acetate or basic lead acetate, barium or ferric chloride, or alum, lakes are obtained, the composition of which is recorded. The compound is also more or less soluble in ethylic or amylic alcohol, acetone, acetic acid, or nitrobenzene.

L. DE K.

Oxidation of Hydrazoximes. II. and III. By GIACOMO PONZIO (*Gazzetta*, 1899, **29**, i, 277—283; 283—292. Compare Abstr., 1898, i, 386). —*Diacetylparachlorophenylhydrazoxime*, $NOH\dot{:}CMe\cdot CMe\dot{:}N_2H\cdot C_6H_4Cl$, obtained by mixing alcoholic solutions of molecular proportions of

isonitrosomethyl ethyl ketone and parachlorophenylhydrazine, forms yellowish needles melting at 180—181°; it is slightly soluble in cold alcohol, light petroleum, or chloroform, and more so in ether; it does not give Pechmann's reaction with sulphuric acid and ferric chloride.

By gently heating dimethylphenylosotriazole with the theoretical quantity of aqueous chlorine, dimethylparachlorophenylosotriazole, $C_2N_3Me_2 \cdot C_6H_4Cl$, is obtained; on treatment with nitric acid, this compound gives dimethylnitrochlorophenylosotriazole,

$$C_2N_3Me_2 \cdot C_6H_3Cl(NO_2),$$
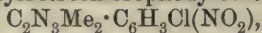
and with chromic acid it yields methylparachlorophenylosotriazole-carboxylic acid, $COOH \cdot C_2N_3Me \cdot C_6H_4Cl$.

Diacetylorthochlorophenylhydrazoxime, prepared from isonitrosomethyl ethyl ketone and orthochlorophenylhydrazine, crystallises from chloroform in nearly colourless, flat needles melting at 189°, and is slightly soluble in the cold, and more so on heating, in alcohol, chloroform, or benzene; it dissolves in cold ether, but is almost insoluble in light petroleum, and gives Pechmann's reaction.

Diacetylparabromophenylhydrazoxime, prepared from isonitrosomethyl ethyl ketone and parabromophenylhydrazine, crystallises from alcohol in lustrous, yellow needles melting at 195—196°, dissolves slightly in the cold and more so on heating in alcohol, chloroform, or light petroleum, and shows Pechmann's reaction. With phosphorus pentachloride, it yields *parabromophenyldimethylosotriazole*, melting at 154—155°, and by dissolving it in cold fuming nitric acid it is converted into *bromonitrophenyldimethylosotriazole;* the latter melts at 119—120°, crystallises from alcohol in lustrous flat needles having a faint yellow colour, and is soluble in cold chloroform or ether.

By heating dimethylphenylosotriazole with the theoretical quantity of iodine and a little water in a sealed tube, dimethylpariodophenylosotriazole is obtained.

Phenyl-3-*methyl*-1:2-*oxypyrro*-1:4-*diazole*, $O{<}{\begin{smallmatrix} CH{-}{-}CMe \\ N \cdot NPh \cdot N \end{smallmatrix}}$, obtained by the action of mercuric oxide on methylglyoxalhydrazoxime, forms large, yellowish prisms melting at 67—67·5° slightly soluble in hot water and more so in hot light petroleum; in all the other ordinary organic solvents, it is soluble in the cold. It is dissolved by mineral acids and is precipitated unchanged by the addition of an alkali; it is not volatile in steam and decomposes when heated to boiling. On passing dry hydrogen chloride into its ethereal solution, no hydrochloride is formed, but partial conversion into chlorophenylmethylosotriazole takes place; hydrogen iodide under the same conditions yields almost exclusively phenylmethylosotriazole, very little of the iodo-derivative being formed. It is reduced by granulated zinc in concentrated hydrochloric acid solution, yielding phenylmethylosotriazole, and by dissolving in cold concentrated nitric acid, *nitrophenyl*-3-*methyl*-1:2-*oxypyrro*-1:4-*diazole*, $O{<}{\begin{smallmatrix} CH{-}{-}CMe{=}N \\ N \cdot N(C_6H_4 \cdot NO_2) \end{smallmatrix}}{>}$ is formed; this crystallises from alcohol in lustrous, yellow needles melting at 136°.

Nitrophenylmethylosotriazole, $C_2N_3HMe \cdot C_6H_4 \cdot NO_2$, prepared by treating phenylmethylosotriazole with concentrated nitric acid, crystal-

lises in thin, yellowish needles melting at 133—134°; it is only slightly soluble in light petroleum, but dissolves in benzene or chloroform even in the cold.

Amidophenylmethylosotriazole, $C_2N_3HMe \cdot C_6H_4 \cdot NH_2$, obtained by reducing the nitro-derivative in alcoholic solution with zinc and hydrochloric acid, crystallises in almost colourless needles melting at 69°, is slightly soluble in water or light petroleum, and more so in the other organic solvents, and is identical with the compound obtained by reducing the nitro-derivative of phenyl-3-methyl-1 : 2-oxypyrro-1 : 4-diazole. By means of the Sandmeyer reaction, the amido-compound readily yields *chlorophenylmethylosotriazole*, $C_2N_3HMe \cdot C_6H_4Cl$, which crystallises in long, thin, lustrous needles melting at 45·5—46° and boiling at 272° under 729 mm. pressure, is volatile in steam and dissolves in the cold in the ordinary organic solvents, but is insoluble in water; it is not oxidised by chromic acid in acetic acid solution, or reduced by hydriodic acid and red phosphorus, but on heating in a sealed tube with dilute hydrochloric acid and potassium dichromate, it is converted into *dichlorophenylmethylosotriazole*, $C_9H_7N_3Cl_2$, which crystallises from alcohol in long, glistening needles melting at 117—118°.

Chloronitrophenylmethylosotriazole, $C_2N_3HMe \cdot C_6H_3Cl \cdot NO_2$, prepared by gently heating chlorophenylmethylosotriazole with nitric acid, crystallises from alcohol in lustrous needles having a very faint yellow tinge, melts at 161—162°, and is soluble in cold chloroform, but only slightly so in cold alcohol, light petroleum, or ether.

Bromophenylmethylosotriazole, $C_2N_3HMe \cdot C_6H_4Br$, obtained when methylphenylosotriazole is shaken with the theoretical quantity of aqueous bromine, crystallises from alcohol in very thin, lustrous needles melting at 64—65°, is soluble in the ordinary organic solvents, and when heated with bromine and water in a sealed tube at 150°, is converted into *dibromophenylmethylosotriazole*, $C_9H_7N_3Br_2$, which separates from alcohol in sparkling laminæ melting at 125—126°.

Iodophenylmethylosotriazole, $C_2N_3HMe \cdot C_6H_4I$, is formed when phenylmethylosotriazole is heated in presence of water with the theoretical proportions of iodine and iodic acid for several days in a sealed tube at 150°; it crystallises from alcohol in white needles melting at 64—65°, and is soluble in cold ether or benzene, but very slightly so in light petroleum. When heated with nitric acid, it yields *iodonitrophenylmethylosotriazole*, $C_2N_3HMe \cdot C_6H_3I \cdot NO_2$, which crystallises from alcohol in long, yellow needles melting at 145—146°, and is soluble in cold ether, but dissolves only slightly in alcohol or light petroleum.

T. H. P.

Isatin V. By Leo Marchlewski and L. G. Radcliffe (*Ber.*, 1899, 32, 1869—1872. Compare Abstr., 1895, i, 288; 1896, i, 96, 235, 449).—*Ethoxyindophenazine*, $\dfrac{C_6H_4 \cdot C:N}{NH—C:N}{>}C_6H_4 \cdot OEt$, prepared by the action of parethoxyorthophenylenediamine on isatin, melts at 225°, dissolves in the ordinary organic solvents, and separates from acetic acid or alcohol in yellow crystals.

Ethoxyorthaminophenimesatin, $\begin{array}{l} C_6H_4 \cdot C : N \cdot C_6H_3(NH_2) \cdot OEt \\ N \!=\!\!=\! C \cdot OH \end{array}$, pre-
pared by the action of parethoxyorthophenylenediamine on acetyl-
pseudoisatin and hydrolysis of the acetate which is first formed,
crystallises from alcohol in glistening, yellow needles and melts at
234—235°; it dissolves easily in hot alcohol, ether, or chloroform, gives
a yellow solution with caustic alkalis, a brown-yellow solution with
concentrated hydrochloric acid, and a red-brown solution with sulphuric
acid, the acid solutions becoming cherry-red on adding ether; it is con-
verted into ethoxyindophenazine on heating with acetic acid, and
quantitatively by heating with concentrated hydrochloric acid at 140°.
Since parethoxyphenylenediamine is not a symmetrical substance, two
formulæ are possible for each of the above compounds, and the
position of the ethoxy-group has not yet been determined.

<div style="text-align:right">T. M. L.</div>

A New Class of Diazo-compounds. Triazolens. By EUGEN
BAMBERGER (*Ber.*, 1899, **32**, 1773—1797).—When diazoindazole
hydroxide (this vol., i, 546) is warmed for a short time with water, it
passes over into an anhydride, $C_6H_4 \!\!<\!\! \begin{array}{c} C \cdot N : N \\ N \!-\!\! N \end{array} \!\!>$,* which the author calls
indazoletriazolen, the four ring system, $CH_2 \!\!<\!\! \begin{array}{c} -N \\ NH \end{array} \!\!>\! N$, being termed a
triazolen ring. Indazoletriazolen is also formed when the diazohydroxide
is shaken with $2N$ hydrochloric acid and the filtered solution treated
with potassium acetate, but it is most readily prepared by the action
of nitrous acid on small quantities of amidoindazole; it forms golden
yellow needles melting at 105·5—106°, dissolves extremely readily in
acetone, acetic acid, chloroform, hot alcohol, or hot water, is only
moderately soluble in ether, and sparingly so in light petroleum. When
heated for any length of time with water or with light petroleum, it is
apt to undergo decomposition. It dissolves with the greatest readi-
ness in dilute mineral acids, forming salts, but is reprecipitated on the
addition of acetates. The *hydrochloride,* obtained by passing hydrogen
chloride into an ethereal solution of indazoletriazolone, or by diazotising
amidoindazole in hydrochloric acid solution, crystallises in yellowish-
white, glistening needles, melts and decomposes at 201·5°, and dissolves
in water, giving a yellow solution. A solution of the hydrochloride in
excess of hydrochloric acid gives a copious scarlet precipitate with bis-
muth-potassium iodide solution, a greenish-black precipitate with a solu-
tion of iodine in potassium iodide, and a white precipitate with
phosphotungstic acid. The *platinochloride,* $(C_7H_4N_4)_2,H_2PtCl_6$, forms a
yellowish, glistening precipitate, and only remains constant in weight
after being kept for several weeks over sulphuric acid. *Indazole-*

* In the original, the formula given is $\begin{array}{c} C_6H_4 \cdot C \cdot N \\ N \!-\!\! N \cdot N \end{array}$, and like formulæ are given for
the other compounds mentioned. As they are, however, all referred to or derived
from indazole, it is to be presumed that the formulæ given in the abstract were
intended.

triazolen-silver nitrate, $C_7H_4N_4,AgNO_3$, crystallises from water in extremely thin, minute needles, and explodes at 210—211°; the *mercurichloride*, $C_7H_4N_4,HgCl_2$, crystallises in yellowish, micro-crystalline needles and decomposes at 170—171°.

Indazoletriazolen unites very readily with aromatic bases or phenols; with β-naphthol, a dye, $N\underset{NH-}{\overset{C_6H_4}{<>}}C\cdot N_2\cdot C_{10}H_6\cdot OH$, *indazolylazo-β-naphthol* is formed when alcoholic solutions of the constituents are mixed; it crystallises in bright red, glistening needles melting and decomposing at about 250°, dissolves in ethylic or amylic alcohol, and also in hot xylene (see following abstract); it is soluble in 6—7 per cent. sodium hydroxide solution, and the *sodium* derivative may be precipitated by the addition of sodium chloride, but is hydrolysed by much water.

Indazolylazodimethylaniline, $N\underset{NH-}{\overset{C_6H_4}{<>}}C\cdot N_2\cdot C_6H_4\cdot NMe_2$, crystallises in dark yellow, glistening needles with a violet lustre, melts at 256—257°, dissolves in concentrated sulphuric acid, and also in $2N$ hydrochloric acid, yielding the hydrochloride in the form of steel-blue, almost black, needles. Dilute potassium hydroxide decomposes indazoletriazolen, a flocculent potassium derivative being formed. Both water and normal sulphuric acid decompose the triazolen, yielding an amorphous product and indazole. It is also decomposed by concentrated hydrochloric acid when the two are boiled vigorously for some 6 hours, the product formed being chlorindazole (this vol., i, 546). The same product may be obtained by adding copper powder or cuprous chloride to a cold solution of indazoletriazolen in concentrated hydrochloric acid. *Iodindazole,* $C_6H_4<\overset{CI}{\underset{N}{\overset{|}{}}}>NH$, is formed when potassium iodide is added to a solution of indazoletriazolen in dilute hydrochloric acid, and is usually accompanied by a considerable quantity of tarry matter; it crystallises from hot, light petroleum in rosettes of glistening needles, melts at 139—140°, and is readily soluble in alcohol, ether, or hot light petroleum.

Boiling hydrobromic acid decomposes indazoletriazolen, yielding a mixture of indazole monobromindazole, dibromindazole, pentabromodiindazole, 3'-bromindazole(?), an acid and basic substance melting at 118—119°(?), and a strongly acid substance melting at 213°. For the separation of these various products, the original must be consulted. The monobromindazole, $C_6H_3Br<\overset{CH}{\underset{N}{\overset{|}{}}}>NH$, melting at 124—125°, and the dibromindazole, $C_6H_2Br_2<\overset{CH}{\underset{N}{\overset{|}{}}}>NH$, are identical with those described by Fischer and Taefel (Abstr., 1885, 541). Although the latter assign the constitution $C_6H_3Br<\overset{CBr}{\underset{N}{\overset{|}{}}}>NH$ to their dibromo-derivative, the author considers such a constitution

impossible, since the compound is insoluble in cold dilute sodium hydroxide. *Pentabromodi-indazole*, $N<^{C_6HBr_3}_{--NH--}>C \cdot C<^{C_6H_2Br_2}_{--NH--}>N$, is soluble in dilute alkali and crystallises from alcohol in colourless, glistening needles melting at 200—200·5°. The substance described as 3'-bromindazole has not been analysed; it crystallises from hot water in needles melting at 144°, and is soluble in dilute alkali.

When indazoletriazolen hydrochloride is boiled with alcohol, nitrogen is evolved, and indazole is formed, the alcohol being simultaneously oxidised to aldehyde.

1 : 3-*Dimethylindazoletriazolen*, $C_6H_2Me_2<^{C \cdot N : N}_{N----N}$, obtained from 3'-amido-1 : 3-dimethylindazole (this vol., i, 544), crystallises in long, golden-yellow, glistening needles melting at 80—81°. During recrystallisation, a small quantity usually decomposes, this decomposition being greater the larger the quantity of material employed. It is readily soluble in most solvents, has a characteristic odour, and gives precipitates with the reagents employed for indazoletriazolen itself.

3-*Methylindazoletriazolen* crystallises in yellow, glistening needles melting at 104·5—105·5° and is readily soluble in the usual solvents.

J. J. S.

Anhydro-formation of β-Naphtholazo-dyes. By Eugen Bamberger (*Ber.*, 1899, **32**, 1797—1802).—When indazoleazo-β-naphthol (see preceding abstract) is warmed with amylic alcohol, it loses the elements of water and becomes converted into the *anhydro*-compound, $C_6H_4<^{C \cdot N : N}_{N----N}>C_{10}H_6$. The reaction is complete after 7 hours boiling, and as the solution cools, golden-yellow, glistening needles of the anhydride are deposited; it melts at 249° without undergoing decomposition, dissolves in concentrated sulphuric or hydrochloric acid, and also in benzene and its homologues, yielding yellowish-green, fluorescent solutions. Other solvents, such as ethylic alcohol, acetic acid, water, chloroform, xylene, cumene, acetone, ether, and light petroleum are also capable of bringing about the anhydroformation, the amount formed depending both on the temperature and the nature of the medium, hydroxylic compounds, as a rule, being the more active.

Dimethylindazolylazo-β-naphthol anhydride,

$$C_6H_2Me_2<^{C \cdot N : N}_{N----N}>C_{10}H_6,$$
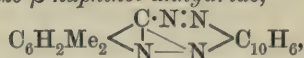
obtained from dimethylindazoleazo-β-naphthol (this vol., i, 545) crystallises in orange-yellow, felted needles melting at 267°, and dissolves in concentrated sulphuric acid, yielding a blue-violet solution.

Attempts to convert phenylazo-β-naphthol into an anhydride proved unsuccessful. J. J. S.

Reduction of Tolualloxazine. By Otto Kühling (*Ber.*, 1899, **32**, 1650—1653. Compare Abstr., 1891, 1342).—By reduction with hydriodic acid, tolualloxazine is converted into *tetrahydrotolualloxazine*,

$C_7H_6{<}{\,}^{NH\cdot CH\cdot NH\cdot CO}_{NH\cdot CH\cdot CO\cdot NH}$, a red, microcrystalline powder which melts above 300°, and is quite insoluble in water, alcohol, ether, or acetone; it dissolves readily in strong acids, but only with difficulty in organic acids; it possesses distinct acidic properties, dissolving in caustic alkalis, alkali carbonates, or in much ammonia, to a yellow solution; an excess of concentrated alkali causes the separation of a white, crystalline salt. The *hydrochloride* separates from concentrated hydrochloric acid in yellow needles.

Dihydrotolualloxazine, to which the formula $C_7H_6{<}{\,}^{NH\cdot CH\cdot NH\cdot CO}_{N=C-CO-NH}$

or $C_7H_6{<}{\,}^{N=C\cdot NH\cdot CO}_{NH\cdot CH\cdot CO\cdot NH}$ is assigned, crystallises in minute, yellow needles, and melts and decomposes above 300°; it dissolves fairly readily in hot water or in alcohol, but not in ether, acetone, or benzene; the aqueous solution is pale yellow, with a blue fluorescence. It does not show basic properties, and is not dissolved by strong acids, but dissolves readily in ammonia, caustic alkalis, and alkali carbonates, giving yellow solutions with a greenish-blue fluorescence. Dilute nitric acid oxidises it to tolualloxazine. T. M. L.

Oxazoles. By MAURICE HANRIOT and G. REYNAUD (*Bull. Soc. Chim.*, 1899, [iii], **21**, 14—18).—*Chloroxazolone* is obtained by passing a current of chlorine through amidomethylethylisoxazole immersed in water, distilling the product with steam, and rectifying the distillate under diminished pressure; it boils at 123° under 30 mm. pressure, and, when heated with hydrochloric acid, yields α-chlorodiethyl ketone. Bromoxazolone, when treated in this way, gives rise to a mixture of α-chloro- and α-bromo-diethyl ketones.

When bromoxazolone is dissolved in cold potash, the bromine is eliminated, and a viscid product is formed; this substance decomposes at 30°, evolving carbonic anhydride; it appears to be the *oxime* of αα-propionylhydroxypropionic acid; its *barium* salt, $BaC_{12}H_{20}N_2O_8$, and *silver* salt, $AgC_6H_{10}NO_4 + H_2O$, have been analysed. Since the oxime is monobasic, it is probably an anhydride, having the constitution $^{C\,Et}_{N\cdot O}{>}CMe\cdot COOK$. When the free acid is allowed to decompose spontaneously, a viscid liquid is obtained, which cannot be distilled even in a vacuum; it appears to be identical with the condensation product obtained from α-chlorodiethyl ketone and hydroxylamine, for both substances, when boiled with hydrochloric acid, are hydrolysed into methyl ethyl diketone (acetylpropionyl), hydroxylamine, and ammonia, and a small amount of the nitrosoketone, $COMe\cdot CEt{:}NOH$. When bromoxazolone is heated with a solution of caustic potash or potassium carbonate, the chief product of the reaction is a substance melting at 182°; it is accompanied by another *compound* melting at 137°, and a small quantity of methyl ethyl diketone. The substance melting at 182° is also produced by the action of mercury or sodium amalgam on bromoxazolone, and from its mode of formation it should

have the constitution $N{<}^{O \cdot CO}_{CEt}{>}CMe \cdot CMe{<}^{CO \cdot O}_{CEt}{>}N$. The compound melting at 137° has the composition $C_{11}H_{16}N_2O_3$, and may be regarded as the condensation product of the anhydride of the oxime of methylethylketole with that of methylethylketolecarboxylic acid.

<div align="right">G. T. M.</div>

Dionine, a new Morphine Derivative. By LUDWIG HESSE (*Chem. Centr.*, 1899 i, 430—431 ; from *Pharm. Centr.-H.*, **40**, 1—5).— *Ethylmorphine hydrochloride* or *dionine*, $OH \cdot C_{17}H_{17}NO \cdot OEt, HCl + H_2O$, is a white, odourless, finely crystalline powder, has a bitter taste, melts at 123—125°, dissolves easily in water, forming a neutral solution, is very slightly soluble in alcohol, insoluble in ether or chloroform, and is precipitated even from dilute aqueous solutions by most alkaloidal reagents. It can scarcely be distinguished from codeine by its colour reactions, but whilst codeine is precipitated from 5 c.c. of a 10 per cent. solution of its hydrochloride by adding a few drops of ammonia solution of sp. gr. 0·91, and is permanently dissolved when 1 c.c. of ammonia is added, ethylmorphine when precipitated in a similar manner is only dissolved by 5 c.c. of ammonia, and the solution after a short time deposits crystals which melt at 93°; this precipitation is evident, even in solutions containing only 1 per cent. Ethylmorphine may be distinguished from morphine by the bluish-green coloration formed when 1 c.c. of a 1 per cent. aqueous solution is treated with a solution of a granule of potassium ferrocyanide in 10 c.c. of water containing a drop of a ferric chloride solution ; morphine under similar conditions gives a dark blue coloration. Ethylmorphine hydrochloride is used as an anodyne and narcotic.

<div align="right">E. W. W.</div>

Solubility of Proteids in Glycerol. By HEINRICH RITTHAUSEN (*J. pr. Chem.*, 1899, [ii], **59**, 479—480).—An historical review.

<div align="right">R. H. P.</div>

Proteids of Wheat-Gluten. By HEINRICH RITTHAUSEN (*J. pr. Chem.*, 1899, [ii], **59**, 474—478).—An historical review of the subject and a criticism of Morishima's work (this vol., i, 466).

<div align="right">R. H. P.</div>

A Slow Proteid Decomposition. By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1899, **27**, 305—316).—Fibrin was infected with putrefactive bacteria, and kept in chloroform water ; it remained sterile for months and even years, but nevertheless underwent solution, proteoses, peptone, and, finally, leucine and tyrosine being formed. This change is believed to be due to an enzyme secreted by the bacteria. Among other points of interest noted, is that a reducing sugar was split off from the proteid during this process.

<div align="right">W. D. H.</div>

Influence of Carbohydrates on the Putrefaction of Proteids. By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1899, **27**, 316—319). —Blood saturated with cane sugar underwent no putrefaction. There was, however, a growth of moulds, which, acting on the sugar, produced alcohol, acetic acid, and ethylic acetate ; the hæmoglobin was consequently changed into acid hæmatin.

<div align="right">W. D. H.</div>

Organic Chemistry.

Action of Chlorine on Propylic Chloride in presence of Anhydrous Aluminium Chloride. By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1899, [iii], 21, 616—623).—By gradually adding anhydrous aluminium chloride to dry propylic chloride kept at 0°, and subsequently heating the liquid to 30—35°, large volume of hydrogen chloride are set free and propylene is formed. This affords a probable explanation of the production of isopropylbenzene when propylic chloride and benzene react in presence of aluminium chloride; the propylic chloride decomposes into propylene and hydrogen chloride, isopropylic chloride being formed by the recombination of these products.

If a brisk current of chlorine is passed through the propylic chloride at 0° to which aluminium chloride is being gradually added, propylenic dichloride is obtained.

On chlorinating propylenic dichloride at 35—40°, aluminium chloride being added little by little, the principal product is $a\beta$-trichloropropane, small quantities of other chloropropanes and of trichlorhydrin being also formed.

When $a\alpha\beta$-trichloropropane is further chlorinated at 80—85° in presence of aluminium chloride, $a\alpha\beta\gamma$-tetrachloropropane and a pentachloropropane which boils at 194—196° and has a sp. gr. 1·614 at 16°, are obtained.   T. H. P.

Chlorobromo-derivatives containing Two Atoms of Carbon. By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1899, i, 588; from *Bull. Acad. roy. Belg.*, 1898, [iii], 36, 519—531).—By the action of antimony pentachloride on tribromethylene dissolved in carbon tetrachloride, $a\beta$-dichloro-$a\alpha\beta$-tribromethane, chlorotetrabromethane, and chlorotribromethylene are formed. *$a\beta$-Dichloro-$a\alpha\beta$-tribromethane* is a colourless liquid, boils at 133° under 35 mm. pressure, boils and decomposes at 210° under the ordinary pressure, solidifies at −5°, has a sp. gr. 2·6263 at 21·5° and a specific refractive index 1·5989 at 15·5°. When boiled with alcoholic potash, it yields *$a\beta$-dichloro-$a\beta$-dibromethylene*, which is a colourless liquid with a pleasant odour, boils at 172° under 765 mm. pressure, solidifies below 0°, has a sp. gr. 2·3753 at 17·5°, a specific refractive index 1·5800 at 16°, and is not attacked by concentrated sulphuric acid. By passing the vapour of $a\beta$-dichloro-$a\beta$-dibromethylene with carbonic anhydride through a red-hot tube, perchlorobenzene, bromine, and chlorine are formed. *$a\beta$-Dichloro-$a\alpha\beta\beta$-tetrabromethane*, prepared by the action of bromine on dichlorodibromethylene dissolved in chloroform, forms large crystals, is soluble in chloroform or benzene, slightly so in alcohol or ether, gives off bromine at 140° and melts at 191°. *$a\beta$-Dichloro-a-bromethylene*, obtained by reducing dichlorotribromethane with zinc dust and alcohol, boils at 112—113°, does not solidify at −20°, has a sp. gr. 1·8764 at 17·5°, a specific refractive index 1·5190 at 16°, and readily combines with bromine to form dichlorotribromethane. From these reactions, the formula of dichloro-
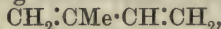
tribromethane is probably $CClBr_2 \cdot CHBrCl$, the antimony pentachloride apparently not affecting the position of the bromine atom as it does in the case of dibromethylene. E. W. W.

Isoprene. By WLADIMIR MOKIEWSKY (*Chem. Centr.*, 1899, i, 589—591; from *J. Russ. Chem. Soc.*, 1898, **30**, 885—900).—Isoprene is most cheaply prepared from turpentine by Tilden's method (Trans., **45**, 413), which yields 1·5—3 per cent. The crude product cannot be purified by fractionating, and towards the end of the distillation it explodes violently; it boils at 30—40°, readily chars, and contains about 50 per cent. of isoprene, the remainder consisting mainly of trimethylethylene. The latter compound has also been found in the isoprene from caoutchouc (Ipatieff and Wittorf, Abstr., 1897, i, 233), and its derivatives were probably confused with amylene derivatives by Berkenheim (*J. Russ. Chem. Soc.*, 1895, **27**, 183), and Bouchardat (Abstr., 1880, 323). According to Faworsky, the combination of isoprene with hypochlorous acid can be used to determine the structure of unsaturated compounds, C_nH_{2n-2}, and the formation of a dichlorhydrin of isoprene-erythritol, $C_5H_8Cl_2(OH)_2$, would indicate the presence of a double linking in isoprene.

By the action of a cold, dilute solution of hypochlorous acid on isoprene, a yellowish-brown, viscous liquid is obtained, from which the *chlorhydrin* of *trimethylene glycol*, $C_5H_{11}ClO$, and the *chlorhydrin* of *isoprene-erythritol* were isolated. The former boils at 141°, has a sp. gr. 1·0562 at 0°/0°, 1·0355 at 22°/22°, and yields an oxide and glycol identical with trimethylene oxide and Eltekoff's glycol respectively. The latter crystallises from alcohol, ether, or benzene, melts at 82·5°, and when heated with water at 120° forms a compound, $C_5H_9Cl \cdot OH$, which melts at 72·5—73°, sublimes readily, and is easily soluble in water or ether. Assuming the formula of isoprene to be
$$CH_2{:}CMe{\cdot}CH{:}CH_2,$$
and that of the chlorhydrin to be $OH \cdot CH_2 \cdot CMeCl \cdot CHCl \cdot CH_2 \cdot OH$ or $OH \cdot CH_2 \cdot CMeCl \cdot CH(OH) \cdot CH_2Cl$, then this compound is probably
$$OH{\cdot}CH_2{\cdot}CMeCl{\cdot}CH{<}{\overset{CH_2}{\underset{O}{}}} \quad \text{or} \quad {\overset{OH{\cdot}CH{-\!-}CH_2}{\underset{CMeCl{\cdot}CH_2}{}}}{>}O.$$
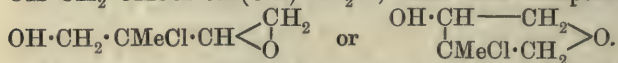
Attempts to obtain the erythritol compound from the ethylic salt of the chlorhydrin also failed. The mother liquor of the chlorhydrin yielded a fraction boiling at 130—160° under 20 mm. pressure, and the residue formed a syrup which boiled at 135—143°. From the former, a small quantity of a crystalline compound was obtained, but even after repeated distillation it contained 41·9 per cent. of chlorine, whilst the amount required for an isomeride of $C_5H_8Cl_2(OH)_2$ is only 41·0 per cent.

By the action of bromine (1 mol.) on a cooled ethereal solution of isoprene, hydrogen bromide is evolved and 65 per cent. of an almost colourless product obtained, which, when distilled, yields two fractions, one boiling at 60—64°, and the other at 90—94°, under 12 mm. pressure. By the action of zinc dust on the former, a hydrocarbon boiling at 36—38° is formed, and this, when dissolved in sulphuric acid and precipitated by potassium carbonate by Wyschnegradsky's method, yields amylic alcohol. Hence Berkenheim's second isoprene

dibromide is really an amylene derivative. The second fraction consists of *isoprene dibromide*, $CMeBr<^{CH_2}_{CHBr}>CH_2$; it is a very unstable liquid, has a penetrating odour, and easily chars. When treated with zinc dust, it yields 70 per cent. of pure isoprene, which is very unstable, boils at 33·5°, and has a sp. gr. 0·6989 at 0°/0° and 0·6794 at 19°/0°. Isoprene dibromide combines with bromine only with difficulty, and when treated with bromine (1 mol.) forms the tetrabromide, $CH_2Br \cdot CMeBr \cdot CHBr \cdot CH_2Br$, but some hydrogen bromide is always liberated. The corresponding *glycol (dibromhydrin)*, $CH_2Br \cdot CMeBr \cdot CH(OH) \cdot CH_2 \cdot OH$ or $OH \cdot CH_2 \cdot CMe(OH) \cdot CHBr \cdot CH_2Br$, prepared by oxidising the dibromide with a 1 per cent. solution of potassium permanganate by Wagner's method, crystallises from hot ether in long, colourless prisms, is odourless, melts at 126·5°, sublimes when heated above the melting point, and by the action of zinc dust is converted into a hydrocarbon. Attempts to prepare the erythritol compound from this glycol resulted only in the formation of substances containing bromine.

The use of hypobromous acid, instead of hypochlorous acid is recommended, on account of its easier preparation and the better yields obtained. The liquid obtained by the action of bromine on mercuric oxide is employed, and the product of the reaction is treated with a small excess of potassium sulphide and filtered. The *isoprene dibromhydrin*, $C_5H_8Br_2(OH)_2$, obtained by treating isoprene with hypobromous acid, crystallises in hexagonal plates and melts at 86°. E. W. W.

A New Hexavalent Hydrocarbon, 2-Methyl-3-hexene-5-ine. By VICTOR GRIGNARD (*Bull. Soc. Chim.*, 1899, [iii], 21, 574—575).—By the action of phosphorus pentachloride on 2 : 3 : 5-methylhexenone, a mixture of a mono- and a di-chloro-derivative, $C_7H_{11}Cl$ and $C_7H_{12}Cl_2$, is obtained. By acting on these two separately with potash and distilling the products at 80 mm. pressure, the fractions passing over below 80°, which possess the alliaceous odour of the acetylene hydrocarbons, give, when mixed and redistilled, a principal fraction boiling at 117—120° under 750 mm. pressure ; it contains a little chlorine, but consists essentially of *2-methyl-3-hexene-5-ine*, $CHMe_2 \cdot CH\!:\!CH \cdot C\!:\!CH$. With ammoniacal cuprous chloride, it gives beautiful, bright yellow flocks of a *copper* compound, $(C_7H_9)_2Cu_2 + H_2O$, which deflagrates violently when heated or when treated with a few drops of concentrated nitric acid ; with Béhal's reagent (saturated alcoholic silver nitrate) it forms thin, white spangles of a *silver* compound, $C_7H_9Ag, AgNO_3$, which detonates on heating and is slightly soluble in alcohol. T. H. P.

2-Methyl-4-heptene-6-ine and 2-Methyl-4 : 5 : 6-heptatriene. By VICTOR GRIGNARD (*Bull. Soc. Chim.*, 1899, [iii], 21, 576—578).—On treating methylheptenone with phosphorus pentachloride, the principal products are two isomerides of the composition $C_8H_{13}Cl$, which, under 10 mm. pressure, boil at 72—75° and 80° respectively. On treating these with potash and purifying, *2-methyl-4-heptene-6-ine*,
$$CHMe_2 \cdot CH_2 \cdot CH\!:\!CH \cdot C\!:\!CH,$$
is obtained as a liquid boiling at 126—129° under 750 mm. pressure

and having a strong alliaceous odour. The addition of ammoniacal cuprous chloride solution precipitates a bright yellow *copper* compound, $(C_8H_{11})_2Cu_2 + H_2O$, which deflagrates violently on heating or on treating with a little concentrated nitric acid. The *silver* compound, $C_8H_{11}Ag,AgNO_3$, obtained by the action of Béhal's reagent, forms nacreous scales which dissolve slightly in alcohol, turn yellow on exposure to light, and detonate on heating.

From a higher boiling fraction of the products of the action of potash on the two chloro-compounds, $C_8H_{13}Cl$, 2-*methyl*-4 : 5 : 6-*heptatriene*, $CHMe_2 \cdot CH_2 \cdot CH \colon C \colon C \colon CH_2$, is obtained as a liquid boiling at 79—82° under 80 mm. pressure and having a strong alliaceous odour more disagreeable than that of its isomeride, 2-methyl-4-heptene-6-ine. It gives no precipitate either with ammoniacal cuprous chloride solution or with Béhal's reagent, but in aqueous alcoholic solution, mercuric chloride gradually forms a white precipitate. When heated with potassium under pressure, the *potassium* derivative is obtained, and this, with Béhal's reagent, gives a precipitate of the *silver* compound, $C_8H_{11}Ag,AgNO_3$. T. H. P.

Theory of the Action of Carbonic Oxide on a Solution of Potassium Ferrocyanide. By Joseph Auguste Muller (*Bull. Soc. Chim.*, 1899, [iii], 21, 472—475).—Carbonic oxide acts on a solution of potassium ferrocyanide according to the equation $K_4FeC_6N_6 + CO + 2H_2O = K_3(CO)FeC_5N_5 + NH_3 + HCOOK$ (see Abstr., 1898, i, 615). The yield increases when an excess of carbonic oxide is used. The reaction, however, is not reversible; the mass action of the carbonic oxide is explained by the fact that it prevents the occurrence of the secondary reaction $4K_3(CO)FeC_5N_5 + 4H_2O = 3K_4FeC_6N_6 + 4CO + (HCOO)_2Fe + 2NH_3$. R. H. P.

Regeneration of Denatured Alcohol by means of Bleaching Powder. By A. and P. Buisine (*Bull. Soc. Chim.*, 1899, [iii], 21, 446—448).—A reply to Duchemin (this vol., i, 666), who states that spirits denatured by the addition of methyl ethyl ketone can be readily recovered by means of bleaching powder. The authors point out that, in 1896, Arachequesne proposed this method of regeneration for ordinary methylated spirits, but it has never been employed. They state also that when it is used with spirits containing methyl ethyl ketone, there is great difficulty in removing all the chloroform formed, and further, the alcohol obtained has a very bad flavour which cannot be got rid of, whilst the presence of chlorine compounds yielding hydrogen chloride, on combustion, prevents its use for burning or lighting. T. H. P.

Derivatives of Nitroethanol [Nitroethylic Alcohol]. By Louis Henry (*Rec. Trav. Chim.*, 1899, 18, 255—266).—β-Nitroethylic alcohol (Abstr., 1898, i, 505) has at the same time the character of an alcohol and of a nitro-compound. As an alcohol, when treated with phosphorus pentachloride, it yields αβ-chloronitroethane, $NO_2 \cdot CH_2 \cdot CH_2Cl$ (*loc. cit.*), which will not condense with formaldehyde, and, when warmed with hydrochloric acid, is decomposed into hydroxylamine hydrochloride and chloracetic acid. It also yields

an *acetate*, $NO_2 \cdot CH_2 \cdot CH_2 \cdot OAc$, which boils at 118—119° under 30—35 mm. pressure, and has a sp. gr. 1·2132 at 11°. *Nitroethylic ether*, $NO_2 \cdot CH_2 \cdot CH_2 \cdot OEt$, can be prepared by heating iodoethylic ether, $CH_2I \cdot CH_2 \cdot OEt$, with silver nitrate; it boils at 178° under 760 mm. pressure, and has a sp. gr. 1·148 at 16°. It cannot, however, be oxidised to nitroacetaldehyde or nitroacetic acid by means of dichromate and sulphuric acid.

As a nitro-compound, it is found to unite with formaldehyde (in 40 per cent. solution) under the influence of a fragment of potassium carbonate ; the product is tertiary nitrotrihydroxybutane (Abstr., 1896, i, 4). With a mixture of piperidine in formaldehyde solution, in which the compound $OH \cdot CH_2 \cdot C_5NH_{10}$ is present, it reacts, forming a *compound*, $OH \cdot CH_2 \cdot C(NO_2)(CH_2 \cdot C_5NH_{10})_2$, which melts at 94—95°. By adding to its ethereal solution either alcoholic sodium ethoxide or metallic sodium, a *sodium* derivative, $NO_2 \cdot CHNa \cdot CH_2 \cdot OH$, can be precipitated.

When nitromethylisopropylcarbinol, $NO_2 \cdot CH_2 \cdot CH(OH) \cdot CHMe_2$ (Abstr., 1898, i, 4) is mixed with a 40 per cent. solution of formaldehyde, and some fragments of potassium carbonate are added, a *compound*, $CHMe_2 \cdot CH(OH) \cdot C(NO_2)(CH_2 \cdot OH)_2$, is formed ; this melts at 103—104°. C. F. B.

Action of Zinc Dust on Bromalcohols. By WLADIMIR MOKIEWSKY (*Chem. Centr.*, 1899, i, 591—592 ; from *J. Russ. Chem. Soc.*, 1898, **30**, 900—903).—When hydrogen bromide is passed into ethylene glycol according to Henry's method (*Ann. Chim. Phys.*, 1872, [iv], **27**, 250), only half the quantity required to form bromethylic alcohol can be used, owing to the crystallisation of the whole mass. When the product is heated, and the gas again passed in, only ethylenic bromide is formed. Henry's ethylene glycol was probably impure. A 60 per cent. yield of bromethylic alcohol is obtained by the action of hypobromous acid (this vol., p. 727) on ethylene. By the action of zinc dust (Gustavson and Demjanoff, *J. Russ. Chem. Soc.*, **20**, 615) on bromethylic alcohol, ethylene is formed. A 65 per cent. yield of *bromamylic alcohol* is obtained by the action of hypobromous acid on trimethylethylene ; this alcohol boils at 45—46° under 12 mm. pressure, has a sp. gr. 1·4104 at 0°/0°, 1·3821 at 21°/0°, and when treated with zinc dust, yields trimethylethylene. E. W. W.

Action of Hydrogen Bromide on Glycols. By WLADIMIR MOKIEWSKY (*Chem. Centr.*, 1899, i, 592 ; from *J. Russ. Chem. Soc.*, 1898, **30**, 904—906).—The crystalline mass obtained by passing hydrogen bromide into ethylene glycol (see preceding abstract) is an additive *compound*, $C_2H_4(OH)_2 + HBr$; it is stable only in an atmosphere of hydrogen bromide, and melts at 50—51°. The corresponding *compound*, $C_3H_6(OH)_2 + HBr$, prepared from trimethylene glycol, melts at 209—210°. When hydrogen bromide is passed into trimethylethylene glycol, more hydrogen bromide is used than is necessary for the formation of a similar additive compound, there is no separation of crystals, and the product consists of two layers. E. W. W.

Preparation of the Higher Aliphatic Amines; Undecyl-amine and Pentadecylamine. By ELIZABETH JEFFREYS (*Amer. Chem. J.*, 1899, **22**, 14—44).—Hofmann's method of preparing aliphatic amines from acid amides does not yield good results in the case of the higher amines, owing to secondary changes occurring, which give rise to aliphatic nitriles and mixed acyl-alkylic carbamides of the type $RNH \cdot CO \cdot NH \cdot CO \cdot R$. The author finds, however, that when bromine is added to a solution of sodium methoxide and any acid amide in methylic alcohol, an aliphatic urethane is formed according to the equation $RCO \cdot NH_2 + Br_2 + 2NaOMe = RNH \cdot COOMe + 2NaBr + MeOH$ (compare Lengfeld and Stieglitz, Abstr., 1893, i, 310 and 631 ; 1894, i, 415) ; on distilling the urethane so obtained with lime, an excellent yield of the corresponding amine is obtained. In order that the best yield of urethane should be obtained by this method, it is necessary to mix the substances together as rapidly as possible ; if the sodium methoxide solution is added gradually to the solution of the amide and bromine, or if the bromine is added drop by drop to the mixture of the amide and the methoxide, a large proportion of a mixed carbamide is formed according to the equation $RCO \cdot NHBr + RCO \cdot NH_2 + NaOMe = R \cdot CO \cdot NH \cdot CO \cdot NHR + NaBr + MeOH$. The formation of mixed carbamides, when the higher amides are submitted to Hofmann's method, is therefore undoubtedly due to the fact that their low solubility in aqueous alkali causes the molecular rearrangement of the acid amide to take place so slowly that the latter is always present in excess.

It is usually assumed that isocyanates are, under ordinary conditions, intermediate products of the Beckmann transformation ; that they are not formed in the rearrangement of acid bromamides in presence of alkali or sodium methoxide appears probable since benzamide, interacting with phenylic isocyanate dissolved in methylic alcohol, invariably gives rise to phenylmethylurethane, without yielding a trace of benzophenylcarbamide. Hoogewerff and van Dorp assumed that bromoformamides are the first products of the same transformation, but since chloroformanilide interacting with benzamide yields hardly a trace of benzophenylcarbamide, their view appears to be discredited.

The new method of preparing urethanes from acid amides is applicable in the case of aromatic amides, but fails with unsaturated compounds of the type $RCH \colon CH \cdot CO \cdot NH_2$, owing to the unsaturated group entering into action.

Further details are given as to palmitic chloramide, methylic pentadecylcarbamate, pentadecylcarbamide, and normal pentadecylamine (Abstr., 1897, i, 315) ; the hydrochloride of the last crystallises in glistening leaflets and decomposes without melting at 200°, whilst the platinochloride decomposes at 205°.
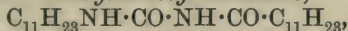
Pentadecylamine pentadecyldithiocarbamate melts at 99°, and, on heating for 20 hours at 100°, is converted into *dipentadecylthiocarbamide*, $(C_{15}H_{31} \cdot NH)_2CS$, which melts at 88·5°. *Pentadecylthiocarbimide*, $C_{15}H_{31} \cdot NCS$, is formed on heating pentadecylamine dissolved in absolute alcohol with an excess of carbon bisulphide during 2

days ; *phenylpentadecylthiocarbamide*, $C_{22}H_{38}N_2S$, prepared from it, crystallises from alcohol and melts at 79°. *Pentadecylcarbamic chloride*, $C_{15}H_{31}NH \cdot COCl$, prepared by heating pentadecylamine hydrochloride with liquid phosgene for 10 hours at 100°, is comparatively stable, and loses hydrogen chloride only slowly when heated at 150° in a stream of air. *Pentadecylic isocyanate*, $C_{15}H_{31}NCO$, melts at 8—14°, *pentadecylphenylcarbamide*, $C_{22}H_{38}N_2O$, at 94°, whilst *dipentadecylcarbamide*, $(C_{15}H_{31} \cdot NH)_2CO$, crystallises from alcohol in small needles and melts at 113°. Pentadecylic alcohol melting at 45—46°, is formed on treating pentadecylamine hydrochloride with boiling aqueous sodium nitrite ; the principal product of this action, however, appears to be the hydrocarbon $C_{15}H_{30}$. *Pentadecylic phenylcarbamate*, prepared from the alcohol and phenylic isocyanate, crystallises from light petroleum in leaflets, melts at 72°, and serves as a means of characterising pentadecylic alcohol.

Methylic heptadecylcarbamate, $C_{17}H_{35} \cdot NH \cdot COOMe$, prepared from stearamide, crystallises from light petroleum or alcohol in leaflets, melts at 63—64°, and is converted almost quantitatively into heptadecylamine (Turpin, Abstr., 1888, 1174) when distilled with lime.

Methylic undecylcarbamate, $C_{11}H_{23} \cdot NH \cdot COOMe$, prepared from lauramide, melts at 45—47°, and can be distilled unchanged under diminished pressure. *Laurylundecylcarbamide*,
$$C_{11}H_{23}NH \cdot CO \cdot NH \cdot CO \cdot C_{11}H_{23},$$
is formed by the action of bromine and sodium methoxide on lauramide, unless the reagents are rapidly brought together ; it crystallises from alcohol in leaflets and melts at 105°. *Normal undecylamine*, $C_{11}H_{23} \cdot NH_2$, melts at 15°, boils at 232° under 742 mm. pressure, and rapidly absorbs water and carbonic anhydride from the air ; the *hydrochloride*, $C_{11}H_{25}N,HCl$, crystallises in lustrous plates and decomposes without melting, and the *platinochloride*, $(C_{11}H_{25}N)_2,H_2PtCl_6$, behaves similarly ; the *benzoyl* derivative, $C_{11}H_{23} \cdot NHBz$, crystallises in needles and melts at 60°, whilst *undecylcarbamide*, $C_{11}H_{23}NH \cdot CO \cdot NH_2$, crystallises from alcohol in prisms and melts at 110°. The action of nitrous acid on normal undecylamine gives rise principally (compare Victor Meyer and Forster, Abstr., 1876, ii, 182 ; 1877, ii, 285) to an *undecylene*, $C_{11}H_{22}$, which boils at 84° under 18 mm. pressure, and yields a *dibromide*, $C_{11}H_{22}Br_2$, boiling at 161° under the same pressure ; only a small quantity of *normal undecylic alcohol*, $C_{11}H_{23} \cdot OH$, is formed, and this melts at 19°, boils at 131° under 15 mm. pressure, and yields undecoic acid on oxidation with potassium dichromate ; *normal undecylic phenylcarbamate*, $C_6H_5 \cdot NH \cdot COO \cdot C_{11}H_{23}$, crystallises from alcohol in needles and melts at 62°.

Ethylic pentadecylcarbamate, $C_{15}H_{31} \cdot NH \cdot COOEt$, prepared by the interaction of sodium ethoxide, bromine, and palmitamide in alcoholic solution, melts at 54° and boils at 225° under 14 mm. pressure.

The action of sodium methoxide and bromine on cinnamide dissolved in methylic alcohol gives rise to a *substance*, $C_{10}H_{12}NO_2Br$, which melts and decomposes at 218°, and possibly has the structure

$CHPhBr\cdot CH(OMe)\cdot CO\cdot NH_2$; salicylamide gives rise under the same conditions to dibromosalicylamide (compare McCoy, this vol., i, 359).

<div style="text-align: right">W. A. D.</div>

Free Chitosamine. By C. A. Lobry de Bruyn and W. Alberda van Ekenstein (*Rec. Trav. Chim.*, 1899, **18**, 77—85. Compare this vol., i, 5, and Breuer, Abstr., 1898, i, 620).—Free chitosamine (glucosamine) is prepared by mixing the hydrochloride with 10—15 times its weight of pure methylic alcohol containing a little more than the calculated quantity of sodium ethoxide. After a quarter of an hour, the solution is filtered from the precipitated sodium chloride; chitosamine, $C_6H_{13}NO_5$, is then deposited, and may be recrystallised from methylic alcohol. Instead of the sodium methoxide, sodium acetate and even sodium nitrite may be used. Chitosamine melts at 105—110°, and has a specific rotation $[a]_D + 44°$ in 0·4 per cent. aqueous solution. In 1 per cent. aqueous solution it is stable, but in 9 per cent. solution it decomposes slowly; it also decomposes in methyl-alcoholic solution, slowly at the ordinary temperature, but more quickly if kept at 32° or boiled for a short time. One product of the decomposition is the ammoniacal derivative of fructose (next abstract but one); others are amido-derivatives of carbohydrates, and from these a mixture of two osazones was prepared which could be separated with alcohol; one of these was *d*-glucosazone.

From chitosamine hydrochloride a mixture of two *pentacetyl* derivatives of chitosamine can be prepared; of these, the less soluble in 50 per cent. alcohol (*a*-compound) melts at 183·5° and is optically inactive, whilst the more soluble (β) melts at 133° and has a specific rotation $[a]_D + 86·5°$ in 2 per cent. chloroform solution.   C. F. B.

A Derivative of *d*-Glucosamine. By B. Sjollema (*Rec. Trav. Chim.*, 1899, **18**, 292—295).—After *d*-glucosamine (Lobry de Bruyn, Abstr., 1895, i, 640) has been boiled for several hours with absolute methylic alcohol, ether precipitates from the solution a hygroscopic substance; this, when washed with moist ether, forms a thick syrup from which crystals deposit when it is allowed to remain. These melt at 132—134°, and have the composition $C_{12}H_{23}NO_{10} + 2H_2O$; their rotation in aqueous solution at 18° changes gradually from $[a]_D - 20·75°$ to about $+ 10$; when boiled with $N/10$ sulphuric acid, they lose all their nitrogen as ammonia, and the solution has then a rotatory power about equal to that of *d*-glucose.   C. F. B.

An Ammoniacal Derivative of Fructose. By C. A. Lobry de Bruyn (*Rec. Trav. Chim.*, 1899, **18**, 72—76).—When fructose (lævulose) is dissolved in methyl-alcoholic ammonia, and the solution is allowed to remain for several months so that air has limited access to it, the optical activity gradually disappears, and a deposit forms which can be recrystallised from hot water. This substance has no definite melting point, but blackens at 210—220°; it has the composition $C_6H_9NO_4$, and the specific rotation is $[a]_D - 75°$ in 0·4 and $- 80°$ per cent. in 1 per cent. aqueous solution. It reduces Fehling's solution on warming, and is reduced by sodium amalgam, but it does not form an

osazone or react with nitrous acid, or yield ammonia when boiled with acids, and it is without basic properties. It forms a *tetracetyl* derivative which melts at 174°, and has a specific rotation $[a]_D - 6.7°$ in 2.4 per cent. chloroform solution. C. F. B.

Formation of Pentabromacetone from Acetonedicarboxylic Acid. By B. BERGESIO and LUIGI SABBATANI (*Chem. Centr.*, 1899, i, 596; from *Ann. Farm. Chim.*, 1898, 529—532).—By the action of bromine on dry acetonedicarboxylic acid or on its aqueous solution, pentabromacetone is formed; it melts at 74°, and when treated with silver nitrate loses 3Br. In Stahre's method of distinguishing citric from tartaric acid, acetonedicarboxylic acid and pentabromacetone are formed as intermediate products. E. W. W.

Action of Reducing Agents on Nitro-Compounds of the Methane Series and their Derivatives. I. A Method of Converting Primary and Secondary Nitro-compounds into the corresponding Oximes, Ketones, and Aldehydes. By MICHAËL I. KONOWALOFF (*Chem. Centr.*, 1899, i, 597—598; from *J. Russ. Chem. Soc.*, 1898, 30, 960—964).—The ketone is prepared from the potassium salt of the nitro-compound by adding an aqueous solution of the latter drop by drop to a solution of stannous chloride in concentrated hydrochloric acid containing 30—50 per cent. more than the theoretical quantity of chloride. The liquid is well shaken, the product distilled in steam, and the ketone separated from the distillate by means of potassium carbonate. Nitrohexamethylene, when treated in this way, yields 80 per cent. of hexamethylene ketone, and by treating the product with sodium carbonate before distilling in steam the oxime is obtained; it melts at 89·5—90·5° and boils at 206—210°. Nitro-octane and nitrodi-isoamyl were treated by this method and phenylnitromethane yields the corresponding aldehyde and oxime. By the action of concentrated hydrochloric acid on salts of nitro-compounds, isonitro-compounds are formed and the latter, when reduced with stannous chloride, yield the oximes. The ketones or aldehydes are prepared by boiling the oximes with acids. E. W. W.

Action of Alkalis on Chloro-ketones and Chlor-alcohols. —By J. SALKIND (*Chem. Centr.*, 1899, i, 596—597; from *J. Russ. Chem. Soc.*, 1898, 30, 906—914).—Trichlorethylideneacetone (anhydrochloralacetone) is prepared by allowing a solution of chloralacetone in concentrated sulphuric acid to remain 12 hours and then pouring the mixture on to ice; this method gives a 75—80 per cent. yield. Trichlorethylideneacetone forms colourless crystals, melts at 25—26°, boils at 93—94° under 20 mm. pressure, is easily soluble in alcohol, ether, benzene, light petroleum, chloroform, or acetone, and insoluble in water. By the action of hydroxylamine (1 mol.) on trichlorethylideneacetone, a small quantity of the *compound*, $C_5H_7Cl_2NO_2$, is formed; it crystallises from benzene in prisms, melts and decomposes at 124—126°, is soluble in alcohol, ether, acetone, hot chloroform, hot light petroleum, or hot benzene, rather sparingly soluble in hot water, and insoluble in carbon bisulphide. By the further action of hydroxylamine on this compound, or by the action

of hydroxylamine (2 mols.) on trichlorethylideneacetone, the *compound*, $C_5H_8Cl_2N_2O_2$, is obtained; it crystallises from a mixture of benzene and alcohol, melts and decomposes at 155°, is easily soluble in alcohol, ether, or acetone, soluble in hot benzene or hot water, rather sparingly soluble in hot chloroform, and insoluble in light petroleum. By the action of a 10 per cent. solution of potassium hydroxide on chloralacetone or on trichlorethylideneacetone, Uschakoff's acid, $C_5H_5ClO_2$ (*J. Russ. Chem. Soc.*, 1897, **29**, 113), is formed. The yield in the former case is 1, in the latter 7 per cent., and 6 per cent. of this compound is also obtained by treating trichlorethylideneacetone with alcoholic potash. A 10 per cent. solution of sodium ethoxide decomposes chloralacetone, but by the action of a 4 per cent. solution, a small quantity of this acid is formed together with an acid syrup. E. W. W.

Mixed Anhydrides of Formic Acid. By AUGUSTE BÉHAL (*Compt. rend.*, 1899, **128**, 1460—1463).—On mixing formic acid and acetic anhydride, in molecular proportions, a certain amount of *formic acetic anhydride* is produced. Its amount may be estimated by acting on the liquid in the cold with a tertiary base such as quinoline, pyridine, or dimethylaniline, which decomposes it with the evolution of carbonic oxide, $COMe \cdot O \cdot COH = CO + MeCOOH$; the volume of the liberated gas gives the quantity of mixed anhydride. The mixture of formic acid and acetic anhydride is distilled, the first portions of the distillate containing the formic acid being rejected; the formic acetic anhydride can then be separated partly by fractional distillation and partly by its slight solubility in light petroleum.

Formic acetic anhydride is a mobile liquid with a strong tear-producing odour; it boils at 29° under 17 mm. pressure, and at ordinary pressures distils and decomposes at 105—120°. It acts on alcohols, giving the corresponding formates and acetic acid, but no trace of the acetates. With ammonia, aniline, methylaniline, para-ethoxyaniline and orthamidophenol, it gives the corresponding formamides, and with urea and phenylhydrazine it yields monoformyl derivatives. T. H. P.

Oxidation of Halogen-substitution Derivatives of Ethylene. By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1899, i, 588—589; from *Bull. Acad. roy. Belg.*, 1898, [iii], **36**, 532—552).—By the action of oxygen on difluorodibromethylene, fluorodibromacetic acid is the only product, and difluorobromacetic acid is not formed (compare Abstr., 1898, i, 457). Fluorotribromethylene, when oxidised by oxygen at 100°, yields fluoropentabromethane and a liquid boiling at 130—160°, which contains ethylic fluorodibromacetate and tribromacetate. By the oxidation of fluorodibromethylene, $CBr_2 \cdot CHF$, *fluorobromacetic bromide*, which boils at 116°, is obtained, together with a small quantity of ethylic dibromacetate and hydrogen fluoride; the two latter are probably formed from dibromacetic fluoride. *Ethylic fluorobromacetate*, $CHBrF \cdot COOEt$, boils at 150°. When perchlorethylene is oxidised with ozone, trichloracetic chloride is formed; it cannot, however, be separated from perchlorethylene by distillation, but the trichloracetamide, prepared by treating the product with ammonia, separates from

boiling chloroform in colourless crystals and melts at 141°. Tribrom-acetamide, prepared from tetrabromethylene in a similar manner, melts at 120°, and dichlorodibromethylene yields a compound which melts at 127°, and is probably chlorodibromacetamide. Per-substituted ethylenes are more or less easily oxidised by oxygen, the most active halogen remaining combined with the CO group. Symmetrical dibrom-ethylene is only very slowly attacked by ozone, yielding a product of complex composition, from which unsymmetrical tetrabromethane, $CBr_3 \cdot CH_2Br$, boiling at 235°, dibromaldehyde boiling at 145°, a small quantity of bromacetic bromide, and an acid were isolated; the last compound boils at 225°, and is probably dibromacetic acid. To account for the oxidation of these compounds, the author inclines to Henry's theory that an unstable ethylenic oxide is formed by direct combina-tion with oxygen.   E. W. W.

Di-isoamylacetic Acid. By H. FOURNIER (*Compt. rend.*, 1899, **128**, 1288—1289).—*Di-isoamylacetic acid*, $CH(C_5H_{11})_2 \cdot COOH$, is obtained by heating di-isoamylmalonic acid at a temperature of about 175°. When crystallised from dilute alcohol or from benzene, it forms white needles which melt at 46—47°, and are insoluble in water, but dissolve readily in organic solvents. *Di-isoamylacetamide*, prepared from the acid chloride, forms silky, white needles which melt at 115°.

Di-isoamylmalonic acid is obtained from its ethylic salt, which is prepared by the action of isoamylic bromide and sodium ethoxide on ethylic isoamylmalonate. It forms white lamellæ which melt at 147—148°, and are very soluble in ether, alcohol, or benzene, but only slightly in carbon bisulphide, and not at all in water.

                                                                C. H. B.

Alternation in Volatility in the Series of the Chlorides of the Normal Acids. By LOUIS HENRY (*Rec. Trav. Chim.*, 1899, **18**, 247—254).—In the series of the chlorides of the normal acids, the boiling point rises by a greater amount in passing from a com-pound with an even number of carbon atoms to the next homologue with an odd number than in the opposite case, as the following table shows; the difference between successive odd members is approxi-

Diff. between even members.	No. of C atoms.	Formula.	Boiling point.	Successive differences.	Diff. between odd members.
	C_2	$CH_3 \cdot COCl$	51— 52°		
48—50°	C_3	$CH_3 \cdot CH_2 \cdot COCl$	78— 80	26—29°	
	C_4	$CH_3 \cdot [CH_2]_2 \cdot COCl$	100—101	20—23	47—50°
44—46	C_5	$CH_3 \cdot [CH_2]_3 \cdot COCl$	127—128	26—28	
	C_6	$CH_3 \cdot [CH_2]_4 \cdot COCl$	145—146	17—19	46—48
48—50	C_7	$CH_3 \cdot [CH_2]_5 \cdot COCl$	174—175	28—30	
	C_8	$CH_3 \cdot [CH_2]_6 \cdot COCl$	194—195	19—21	45—46
	C_9	$CH_3 \cdot [CH_2]_7 \cdot COCl$	220	26	
	C_4	$CHMe_2 \cdot COCl$	92		—
49—50	C_5	$CHMe_2 \cdot CH_2 \cdot COCl$	113—114	21—22	
	C_6	$CHMe_2 \cdot [CH_2]_2 \cdot COCl$	141—142	27—29	—

mately equal, as is that between successive even members, and, moreover, the two differences are equal.

The corresponding alcoholic chlorides ($R \cdot CH_2Cl$ instead of $R \cdot COCl$) exhibit no such alternation. Three acid chlorides containing an isopropyl group exhibit a similar alternation, however, except that here the greater increase is from odd to even, as seen in the lower section of the table.

Similar alternations have long been observed in the case of melting points; this appears to be the first instance in the case of boiling points.   C. F. B.

Vinylacetic Acid. By Johannes Wislicenus (*Ber.*, 1899, **32**, 2047—2048).—β-Bromoglutaric acid (Ssemenoff, *J. Russ. Chem. Soc.*, 1899, **31**, 115), obtained when the β-hydroxy-acid is heated with saturated hydrobromic acid at 100° in sealed tubes, forms crystalline plates melting at 137°. When neutralised with aqueous sodium hydroxide and the solution warmed, carbonic anhydride is evolved and the solution becomes acid. When dilute sulphuric acid is added, the mixture submitted to distillation in steam, and the distillate extracted in a Hagemann's apparatus, a syrupy *acid* is obtained. The *calcium* salt of this acid crystallises in colourless plates having the composition $(C_4H_5O_2)_2Ca + H_2O$. From its method of preparation, it is concluded that the acid must be vinylacetic acid, and it follows that the acid obtained from ethylenemalonic acid and described by Fittig and Roeder (Abstr., 1885, 653) as vinylacetic acid, but by Perkin (Trans., 1885, 815) as trimethylenecarboxylic acid, cannot be vinylacetic acid, since its calcium salt crystallises with $6H_2O$.   J. J. S.

Oxymethylene Derivatives of Alkylic Cyanacetates. By E. Grégoire de Bollemont (*Compt. rend.*, 1899, **128**, 1338—1341).—When amylic formate acts on dry ethylic sodiocyanacetate at 100°, it yields sodium ethylic formylcyanacetate, and if this is treated with barium chloride, the salt $Ba[O \cdot CH:C(CN) \cdot COO \cdot C_5H_{11}]_2$ is obtained in nacreous leaflets very soluble in alcohol, but only very slightly so in ether. The corresponding silver salt is a crystalline, white powder slightly soluble in hot water, from which it crystallises in groups of small needles.

When amylic cyanacetate and ethylic orthoformate are treated with acetic anhydride, *amylic ethoxymethylenecyanacetate*,

$$OEt \cdot CH:C(CN) \cdot COO \cdot C_5H_{11},$$
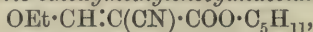
is obtained; it boils at about 211° under 35 mm. pressure. The *ethylic* compound forms white needles which melt at about 52° and dissolve readily in alcohol and in ether; the *methylic* compound forms elongated tablets which melt at about 34° and are very soluble in alcohol. The barium salt, obtained by the action of barium hydroxide on the amylic, ethylic, or methylic compound, is identical with that obtained from the product of the action of amylic formate on ethylic sodiocyanacetate.

Methylic orthoformate behaves in the same way as the ethylic compound in these reactions. *Methylic methoxymethylenecyanacetate,*

$OMe \cdot CH \colon C(CN) \cdot COOMe$, forms slender, transparent needles which melt at about 88°, whilst *ethylic methoxymethylenecyanacetate* forms transparent rhombs which melt at about 99°.   C. H. B.

Reaction between Aliphatic Thiocyanates and Metallic Derivatives of Ethylic Acetoacetate and Analogous Substances. By ELMER P. KOHLER (*Amer. Chem. J.*, 1899, 22, 67—80). —When ethylic cupracetoacetate dissolved in absolute alcohol is heated with ethylic thiocyanate (1 mol.), copper mercaptide is precipitated, and a mixture of ethylic bisulphide, ethylic acetoacetate, and *ethylic cyanocupracetoacetate*, $(C_7H_8O_3N_2)_2Cu$, obtained; the last crystallises from alcohol, in which it is sparingly soluble, in small, dark green plates, and, unlike ethylic cupracetoacetate, is not decomposed by boiling with water or alcohol, although, when warmed with dilute sulphuric acid, it readily yields ethylic cyanacetate. It appears probable that in this reaction ethylic cyanacetate and the copper derivative, $(Et_2S)_2Cu$, of ethylic disulphide are initially formed, and that the ethylic cyanacetate then interacts with ethylic cupracetoacetate, forming ethylic acetoacetate and cupricyanacetate; the ethylic bisulphide is formed by its copper derivative undergoing decomposition to form copper mercaptide. Methylic, propylic, isopropylic, and benzylic thiocyanates interact with ethylic cupracetoacetate in the same manner as ethylic thiocyanate.

Ethylene dithiocyanate interacts with cold alcoholic ethylic cupracetoacetate to form *copper thiocyanomercaptide*, $CNS \cdot CH_2 \cdot CH_2 \cdot SCu$, and *symmetrical dithiocyanethylic bisulphide*, $(CNS \cdot CH_2 \cdot CH_2 \cdot S)_2$; the former is a white, insoluble solid which slowly dissolves in boiling concentrated hydrochloric acid, yielding *iminotrimethylenebisulphide hydrochloride*, $\begin{matrix} CH_2 \cdot S \\ | \\ CH_2 \cdot S \end{matrix} \bigg> C \colon NH, HCl$, and is oxidised by fuming nitric acid to 1 : 2-ethanedisulphonic acid. Symmetrical dithiocyanethylic bisulphide, best prepared by shaking copper thiocyanomercaptide with water and iodine, is a colourless liquid which does not solidify at $-20°$, and, when warmed with concentrated caustic potash, gives rise to ethylene tetrasulphide; it does not interact with ethylic cupracetoacetate in the cold, but at the temperature of boiling alcohol yields ethylic cupricyanacetoacetate, and a mixture of several sulphur compounds. This explains the complexity of the product obtained on heating ethylenic dithiocyanate with alcoholic ethylic cupracetoacetate. When ethylenic dithiocyanate (1 mol.) is gradually added to a boiling solution of ethylic cupracetoacetate in absolute alcohol, both of the thiocyano-groups enter into action, and ethylenic tetrasulphide is formed together with ethylic cupricyanacetoacetate, ethylic acetoacetate, and the copper derivative, $C_2H_4S_2Cu_2$, of ethylene mercaptan.

$\alpha\beta$- and $\alpha\gamma$-Dithiocyanopropane interact with ethylic cupracetoacetate in the same manner as ethylene dithiocyanate. Methylene thiocyanate yields a dark brown, insoluble *product*, $CH_2S_2Cu_2$, probably *copper methylene mercaptide*, but possibly a mixture of cuprous sulphide and the *mercaptide*, $(SCu \cdot CH_2 \cdot S)_2$; the latter assumption would account for its evolving hydrogen sulphide and giving rise to a

light yellow powder, $C_2H_4S_3Cu_2$, when left in contact with concentrated hydrochloric acid.

Ethylic thiocyanate does not interact as definitely with ethylic sodacetoacetate as with ethylic cupracetoacetate; this is due to the soluble mercaptide produced decomposing the ethylic acetoacetate and cyanacetoacetate initially formed. The best results are obtained by leaving dry ethylic sodacetoacetate in contact with an excess of ethylic thiocyanate in cold absolute ether, when 60 per cent. of the theoretical yield of ethylic cyanacetoacetate is obtained. From ethylic sodethylacetoacetate, under similar conditions, *ethylic cyanethylacetoacetate*, $C_9H_{13}O_3N$, was obtained as an oil boiling at 130° under 35 mm. pressure.

Whereas ethylic cupracetoacetate interacts with chlorethylic thiocyanate in the same manner as with ethylic thiocyanate, the chlorine atom present being without influence, ethylic sodacetoacetate gives rise principally to *ethylic thiocyanethylacetoacetate*, $CNS \cdot CH_2 \cdot CH_2 \cdot CHAc \cdot COOEt$, which crystallises from light petroleum in colourless plates or needles and melts at 83°; a considerable proportion of ethylic cyanosodacetoacetate is, however, also formed.   W. A. D.

Relations between the Melting Points and Molecular Weights of the Normal and Non-normal Acids of the Oxalic Acid Series. By Gustave Massol (*Bull. Soc. Chim.*, 1899, [iii], **21**, 578—580, and 580—583).—From the melting points collected in the following table:

C_2	Oxalic acid	212°	C_3	Malonic acid	132°
C_4	Succinic acid	180	C_5	Glutaric acid	97
C_6	Adipic acid	148	C_7	Normal pimelic acid	103
C_8	Suberic acid	140	C_9	Normal azelaic acid	117·5
C_{10}	Sebacic acid	127			

it is seen that for the normal acids of the oxalic acid series, (1) each term of the even series melts at a higher temperature than either of its two contiguous homologues of the odd series, and (2) the odd series shows a minimum melting point for the C_5 acid, as is the case for the normal fatty acids.

Among the non-normal acids of this series, very few comparable data are known. The most complete series is that of the malonic acids mono-substituted with a normal lateral chain:

	Even.	Odd.
C_4 Methylmalonic acid	130°	—
C_5 Ethylmalonic acid	—	111·5°
C_6 Normal propylmalonic acid	93·5	—
C_7 Normal butylmalonic acid	—	98·5
C_8 Normal pentylmalonic acid	82	—
C_{10} Normal heptylmalonic acid	97·5	—

This series shows a minimum melting point, which is also that of the acid with C_5 in the lateral chain, and further, it is seen that an acid of the even series melts at a lower temperature than either of its two contiguous homologues in the odd series. Other series are given,

but are very incomplete, and in all of them the melting point falls as the molecular weight increases. T. H. P.

Stability of Solutions of Oxalic Acid. By W. P. JORISSEN (*Zeit. angew. Chem.*, 1899, 521—525).—A sterilised normal solution of oxalic acid suffered no decomposition in the dark, even after 101 days, but when exposed to the light it lost, in 57 days, so much acid that its strength was reduced from N 0·99 to N 0·965; after 101 days exposure, this was reduced to N 0·926. A solution containing 10 grams of oxalic acid and 50 c.c. of sulphuric acid per litre also kept well in the dark, but exposure to light for 37 days reduced its strength from 0·1592 to 0·1420. A solution containing 10 grams of oxalic and 1 gram of boric acid per litre did not suffer any diminution of strength in the dark, but in the light its strength was reduced from 0·1592 to 0·1523 in 37 days. A centinormal solution of oxalic acid containing also 1 gram of boric acid per litre did not lose in strength in the dark, but when exposed to the light its acidity was reduced from 0·01002 to 0·002, and after 78 days to *nil*.

A centinormal solution of oxalic acid mixed with mould (which had been cultivated on moist bread) was reduced in strength from 0·00992 to 0·00927 when kept in the dark for 62 days; in a second experiment, the acid completely disappeared when kept in the dark for 56 days. The mould has, however, no appreciable action on decinormal or centinormal solutions when these contain in addition 50 c.c. of sulphuric acid per litre. A centinormal solution containing 1 gram of boric acid per litre and mixed with the mould was reduced in strength from 0·01002 to 0·00711 when kept in the dark, in winter time, for 62 days; from 0·0100 to 0·00926 at the summer temperature in 56 days. When 2 grams of boric acid were used, there was no loss when kept for 62 days in winter time, but 44 days exposure in summer time reduced the strength from 0·01010 to 0·00916. Addition of alcohol was also tried, a decinormal solution of oxalic acid in water containing 12·4 per cent. of alcohol being exposed for 36 days in the dark, when the strength had diminished from 0·0984 to 0·0931; when exposed to the light, it diminished from 0·0984 to 0·0716; addition of twice the amount of alcohol gave no better results. The action in the dark is probably due to the formation of ethylic oxalate.

Further experiments are appended showing that sulphuric and boric acids increase the velocity of oxidation of oxalic acid in the light. A remarkable action is exercised by manganous sulphate, for this salt, whilst acting as a preservative in the light, actually promotes the oxidation of the acid in the dark. L. DE K.

Action of Acidic Metallic Oxides on Organic Acid. By ARTHUR ROSENHEIM (*Zeit. anorg. Chem.*, 1899, 21, 1—18).—*Decomposition of aluminium, chromium, and iron oxalates with metallic chlorides* [with MAX PLATSCH.]—A concentrated solution of ammonium aluminium oxalate, $Al(CO_2 \cdot COO \cdot NH_4)_3 + 2\frac{1}{2}H_2O$, when treated with the equivalent quantity of barium chloride, yields a large quantity of barium oxalate if the barium chloride is added all at once. If, however, the barium chloride is added gradually, only a very small precipitate is obtained, and the filtrate after a time deposits the *double* salt,

$Al(C_2O_4)_3BaNH_4 + 2H_2O$, in silky, white needles. This salt is much more unstable than the alkali aluminium oxalates, and decomposes when treated with warm water into barium oxalate and aluminium oxalate, whereas the alkali aluminium oxalates crystallise from boiling water without decomposition. With strontium chloride, the ammonium aluminium oxalate yields a small quantity of strontium oxalate, and the *salt*, $Al(C_2O_4)_3SrNH_4 + 5H_2O$, which is not so stable as the preceding barium salt. With calcium, magnesium, and zinc chlorides, the ammonium aluminium oxalate is completely decomposed. With cobalt chloride, cobalt oxalate is first precipitated, then the double salt, $NH_4CoCl_3 + 6H_2O$, and finally the salt $(NH_4)_2O,Al_2O_3,4C_2O_3$, mixed with a small quantity of ammonium chloride. A similar reaction takes place with nickel, cadmium, or copper chloride.

The blue ammonium chromoxalate, $Cr(CO_2 \cdot COO \cdot NH_4)_3,3H_2O$, when treated with barium chloride, yields a small quantity of barium oxalate, and the *salt* $[Cr(C_2O_4)_3]_2Ba_3 + 14H_2O$, which crystallises in bluish-green needles, and is decomposed by warm water. With strontium chloride, it yields a large quantity of strontium oxalate, and the *salt* $Cr(C_2O_4)_3SrNH_4 + 5H_2O$, which crystallises in bluish-green needles, and is very unstable. With calcium, magnesium, or zinc chloride at ordinary temperatures, decomposition takes place with the formation of metallic oxalates, ammonium chloride, and acid chromium oxalate; but with calcium chloride at $-15°$, the *double* salt, $Cr(C_2O_4)_3CaNH_4$, is obtained, which crystallises in needles, and at the ordinary temperature at once decomposes, yielding calcium oxalate. With cobalt, nickel, or copper chloride, a reaction takes place similar to that obtained with ammonium aluminium oxalate and the metallic oxalates; metallic ammonium chlorides and the red ammonium chromoxalate are produced. With cadmium chloride, cadmium oxalate and cadmium ammonium chloride crystallise out first, and the mother liquors yield the *salt* $Cr(C_2O_4)_3CdNH_4 + 10H_2O$, which crystallises in dark blue prisms.

The red potassium chromoxalate, $C_2O_4Cr \cdot C_2O_4K + 5H_2O$, when treated with barium chloride, yields the *double* salt $Cr(C_2O_4)_3BaK + 2H_2O$, which crystallises in bluish-green needles. The mother liquors yield a non-crystallisable syrup free from oxalic acid. With strontium chloride, a similar reaction takes place, and the *salt* $Cr(C_2O_4)_3SrK + 4H_2O$ is obtained. With calcium, magnesium, copper, or cadmium chlorides no reaction takes place.

Ammonium ferrioxalate, $Fe(C_2O_4 \cdot NH_4)_3,3H_2O$, yields, with barium chloride, a considerable quantity of barium oxalate, and the *salt* $[Fe(C_2O_4)_3]_2Ba_3 + 22H_2O$. With strontium chloride, it yields a larger quantity of strontium oxalate, and the *salt* $Fe(C_2O_4)_3SrNH_4 + 6H_2O$. With calcium chloride and other metallic chlorides, complete decomposition takes place.

Salts of Molybdanumoxalic and Vanadiumoxalic Acids [with HERMANN ITZIG.]—*Sodium molybdanumoxalate*, $\begin{matrix} CO \cdot O \\ CO \cdot O \end{matrix} > MoO(ONa)_2 + 3H_2O$, is obtained by adding the theoretical quantity of molybdic acid to a boiling solution of sodium oxalate, and after concentrating to a syrup on the water-bath, allowing the mixture to crystallise over sulphuric

acid; it crystallises in white, interlacing needles, and is very soluble. The *salt* $C_2O_4(MoO_2 \cdot ONa)_2 + 6H_2O$, obtained by saturating a boiling solution of sodium oxalate with molybdic acid, separates in white, microscopic crystals. The corresponding *barium* salt with $3\frac{1}{2}H_2O$, obtained by shaking barium oxalate suspended in water with the theoretical quantity of molybdic acid at the ordinary temperature for 3—4 hours, crystallises in white needles and dissolves in water at $50°$, but on keeping the solution, decomposition occurs with the formation of barium molybdate and barium oxalate.

Barium vanadium oxalate, $Ba_3V_2O_5(C_2O_4)_4 + 15H_2O$, is obtained by treating ammonium vanadium oxalate with barium chloride, crystal-lises in small, yellow needles, and is sparingly soluble in water.

[With IVAN KOPPEL.]—A table of the electric conductivity of the salts of the complex oxalic acids is given.   E. C. R.

Potassium Plato-oxalonitrite. By MAURICE VÈZES (*Bull. Soc. Chim.*, 1899, [iii], **21**, 481—487).—This double salt has been already fully described (Abstr., 1898, i, 64). It forms monoclinic prisms $[a : b : c = 0.4131 : 1 : 0.3340 ; \beta = 111° 39' 51'']$.   R. H. P.

A Lower Homologue of Citric Acid. By AUGUSTIN DURAND (*Compt. rend.*, 1899, **128**, 1525—1527).—By a method similar to that employed by Haller and Held for preparing citric acid synthetically (Abstr., 1891, 178), the author has obtained the next lower homologue, namely, $COOH \cdot C(OH)(COOH) \cdot CH_2 \cdot COOH$. A mixture of an ethereal solution of ethylic oxalacetate with potassium cyanide and hydro-chloric acid gives the cyanhydrin $COOEt \cdot C(OH)(CN) \cdot CH_2 \cdot COOEt$, which, on hydrolysis, yields $COOEt \cdot C(OH)(COOH) \cdot CH_2 \cdot COOEt$. The *acid*, obtained by decomposing the lead salt with hydrogen sulphide, forms a light yellow syrup with a taste resembling that of citric acid. On neutralising the acid with lime water, the *calcium* salt is slowly deposited in mammillary tufts of shining, white crystals containing $5\frac{1}{2}H_2O$. The *zinc* salt is precipitated as a white powder.   T. H. P.

Preparation of Mucobromic and Mucochloric Acids. By HUGO SIMONIS (*Ber.*, 1899, **32**, 2084—2086. Compare Schmelz and Beilstein, *Annalen, Supp.*, **3**, 276; Jackson and Hill, Abstr., 1878, 402; 1879, 224).—Mucobromic acid is best obtained in large quantities by the following process:—Furfuraldehyde is covered with about 10 times its weight of water and is then treated with 10 times its weight of bromine, which is run in fairly quickly; the reaction is violent and is completed by boiling the mixture for at least about 15 minutes. When the solution is evaporated to a small bulk, the acid separates out and may be recrystallised from hot water. The yield is nearly theoretical. Mucochloric acid may be obtained in a similar manner by using fur-furaldehyde, manganese dioxide, and hydrochloric acid.   J. J. S.

Derivatives of Cyclopentane and of Dipentamethenyl. By WILHELM MEISER (*Ber.*, 1899, **32**, 2049—2057).—Wislicenus's cyclo-pentanol (Abstr., 1893, i, 556) reacts with an alcoholic solution of phenylcarbimide, yielding the *phenylurethane*, $C_5H_9 \cdot O \cdot CO \cdot NHPh$, which

crystallises from alcohol in colourless needles melting at 132·5°. A good yield of cyclopentene (*loc. cit.*) may be obtained by the action of alcoholic potash on bromocyclopentane, a small amount of *pentamethenylic ethylic ether*, $C_5H_9 \cdot OEt$, being also formed; the latter is a colourless liquid boiling at 126—127°. *Cyclopentanediol*, $C_5H_8(OH)_2$, obtained when cyclopentene dibromide is boiled with potassium carbonate solution, is an extremely hygroscopic, crystalline solid distilling at 226·5—227° under ordinary atmospheric pressure, or at 126·5—127·5° under 12 mm. pressure; when freshly distilled, it melts at 48—49·5°, is readily soluble in alcohol or water, and has a sweet odour. The *diacetate*, $C_5H_8(OAc)_2$, is a thick liquid boiling at 224—226°; the *diphenylurethane*, $C_5H_8(O \cdot CO \cdot NHPh)_2$, crystallises from benzene in minute, colourless needles melting at 211—212° and is sparingly soluble in the usual solvents. 2-*Chlorocyclopentanol*, $C_5H_8Cl \cdot OH$, obtained by leading dry hydrogen chloride into the glycol heated at 170—190°, is a colourless oil distilling at 78° under 13 mm. pressure and volatile in steam; it is also formed by the addition of hypochlorous acid to cyclopentene, and yields a *phenylurethane*, $C_5H_8Cl \cdot O \cdot CO \cdot NHPh$, crystallising in colourless needles and melting at 107—108°. When the chlorhydrin is heated with concentrated aqueous potassium hydroxide, water and *cyclopentenic oxide*, C_5H_8O, distil over. This is a colourless oil with an unpleasant odour; it distils at 102°, and in many properties resembles ethylenic oxide, but its oxygenated ring is even more readily broken than that of ethylenic oxide; for example, the oxide combines with hydrogen chloride instantaneously at $-18°$, yielding the original chlorocyclopentanol.

Dipentamethenylpinacone, $C_4H_8 {:} C(OH) \cdot C(OH) {:} C_4H_8$, may be isolated from the reduction products of cycloketopentane, if the alcohol, $C_5H_9 \cdot OH$, is first distilled off under atmospheric pressure, the residue then submitted to distillation under reduced pressure, and the fraction passing over at 130—160° under 17 mm. pressure collected separately. After crystallisation from a mixture of benzene and light petroleum, it forms colourless, glistening pyramids melting at 106·5—108°. The residue left after the pinacone has been distilled consists of the *anhydride*, $C_{20}H_{32}O_2$, of the pinacone and crystallises in glistening needles melting at 161·3—162·3°. When the pinacone is warmed with dilute sulphuric acid, it loses water and becomes transformed into the *pinacolin*, $\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} {>} C {<} \begin{matrix} CH_2 \cdot CH_2 \\ CO - CH_2 \end{matrix} {>} CH_2$; this is a pale yellow, somewhat thick oil distilling at 105—108° under 19·5 mm. pressure; it has a strong odour of peppermint, is volatile with steam and readily reacts with bromine or potassium permanganate. The *oxime*, $C_{10}H_{16} {:} N \cdot OH$, crystallises in plates and prisms melting between 55° and 60°, and according to the author is probably a mixture of stereoisomeric forms. When oxidised with nitric acid, the pinacolin yields carbonic anhydride and succinic acid, but the chief product is a syrupy dibasic *acid*, $C_{10}H_{16}O_4$, the silver salt of which, $C_{10}H_{14}O_4Ag_2$, has been prepared and analysed. The conversion of the pinacone into the pinacolin is interesting as it is one of the first cases observed of the conversion of a pentacyclic into a hexacyclic carbon compound.

Dipentamethenyl, $C_5H_9 \cdot C_5H_9$, obtained by the action of sodium on

an ethereal solution of bromocyclopentane, is a colourless oil boiling at
189—191°. **J. J. S.**

Cyclic Isomeric Change of Acetylmethylheptenone. By
GEORGES LESER (*Bull. Soc. Chim.*, 1899, [iii], **21**, 546—549. Com-
pare Abstr., 1898, i, 512, and this vol., i, 479).—When acetylmethyl-
heptenone is allowed to remain for two hours with six times its weight
of 80 per cent. sulphuric acid, and is then diluted with water and
extracted with ether, the isomeric 2-*acetyl*-1 ›1-*dimethylcyclohexanone*-3,
$CMe_2 {<}^{CHAc \cdot CO}_{CH_2-CH_2}{>} CH_2$, is obtained as an oil having a penetrating
smell and boiling at 110—111° under 12 mm. pressure. Its alcoholic
solution gives a violet-red coloration with ferric chloride, and it forms
a *semicarbazone* melting at 168°. With aqueous potash, it yields
1 : 1-*dimethylcyclohexanone*-3, which boils at 173—174°, and yields a
semicarbazone melting at 198°. 2-Acetyl-1 : 1-dimethylcyclohexan-
one-3, on treatment with alcoholic potash, yields a *ketonic acid*,
$COMe \cdot CH_2 \cdot CMe_2 \cdot [CH_2]_3 \cdot COOH$, which boils at 190—191° under 20
mm. pressure, yields an *oxime* melting at 101—101·5° (not at 98° as
previously described, *loc. cit.*) and a *semicarbazone* melting at 161°.
On treatment with bromine and caustic soda, it is oxidised to normal
$\beta\beta$-dimethylpimelic acid, which forms long prisms melting at 104°
(101—102·5°, according to von Baeyer), and on distillation with soda-
lime, is reconverted into 1 : 1-dimethylhexanone-3. **R. H. P.**
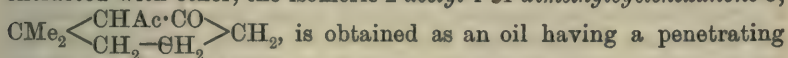
**Action of Ferric Chloride and Bromide on Aromatic
Hydrocarbons and their Haloid Substitution Derivatives.**
By VICTOR THOMAS (*Compt. rend.*, 1899, **128**, 1576—1578. Compare
Abstr., 1898, i, 640, and this vol., i, 26).—In addition to the products
of the action of ferric chloride on paradibromobenzene already men-
tioned (*loc. cit.*), the author has now separated parabromochloro-
benzene, already prepared by Griess and Körner, and two trichloro-
bromobenzenes melting at 93° and 138° respectively, and crystallising
in slender needles, which readily sublime and are soluble in the
ordinary organic solvents.

Iodo-derivatives of aromatic hydrocarbons are readily chlorinated
by ferric chloride, iodobenzene, for example, giving parachloriodo-
benzene, hydrogen chloride being evolved in large quantities; with
di-iodobenzene, the action is even more energetic, iodine being freely
liberated, and chloriodo-derivatives containing only 1 atom of iodine in
the molecule being formed.

In general, ferric bromide acts on aromatic hydrocarbons in a similar
manner to, but less energetically than, the chloride. With benzene,
the action is very slow at ordinary temperatures, but becomes very
rapid on boiling for some hours, the mass carbonising and bromobenz-
enes being formed. In the case of toluene, the action begins at about
60°, and continues steadily on boiling, less charring and better
yields of the bromo-derivatives being obtained than with benzene.

Chlorinated benzenes are rapidly attacked by ferric bromide, chloro-
benzene giving the parachlorobromo-compound. With more highly

chlorinated benzenes, the whole series of chlorobromo-derivatives can be obtained. The intensity of the action decreases as the number of chlorine atoms in the molecule increases.

On heating mono- or di-iodobenzene with ferric bromide, the iodine is entirely replaced, paradibromobenzene being formed in both cases.

T. H. P.

Derivatives of Symmetrical Trichlorobenzene. By C. LORING JACKSON and F. H. GAZZOLO (*Amer. Chem. J.*, 1899, **22**, 50—60).— 1 : 3 : 5-*Trichloro*-2-*iodobenzene*, prepared from 2 : 4 : 6-trichloraniline (V. Meyer and Sudborough, *Ber.*, 1894, **27**, 3151) by means of the diazo-reaction, crystallises from alcohol in slender, white needles, melts at 55°, sublimes easily, and is apparently not acted on by concentrated mineral acids or alkalis ; when warmed, however, with alcoholic sodium ethoxide, iodine is removed, and trichlorobenzene formed. In this respect, 1 : 3 : 5-trichloro-2-iodobenzene resembles the corresponding tribromiodobenzene (Jackson and Calvert, Abstr., 1896, i, 473), and, like the latter, does not interact with boiling aniline, aqueous caustic soda, or ethylic sodiomalonate ; when warmed, however, with a mixture of nitric and sulphuric acids, it gives rise to 1 : 3 : 5-trichloro-2 : 4-dinitrobenzene, iodine being liberated.

1 : 3 : 5-*Trichloro*-2-*bromobenzene*, prepared from 2 : 4 : 6-trichloraniline, crystallises from alcohol in white, radiating needles, melts at 64—65°, readily sublimes, and is not acted on by concentrated mineral acids ; when warmed, however, with a mixture of sulphuric acid and nitric acid of sp. gr. 1·52, it yields 1 : 3 : 5-*trichloro*-2-*bromo*-4 : 6-*dinitrobenzene*, which crystallises from a mixture of alcohol and benzene in rhombic plates, melts at 175°, and readily sublimes. This, when warmed with aniline, gives rise to 2-bromo-4 : 6-dinitro-1 : 3 : 5-tri-anilidobenzene (Jackson and Bancroft, Abstr., 1890, 982), whilst, left in contact with cold, alcoholic sodium ethoxide (3 mols.), it is converted into *bromodinitrodiethoxybenzene* [$OEt_2 : Br : (NO_2)_2 = 1 : 3 : 2 : 4 : 6$ or $1 : 5 : 2 : 4 : 6$], which crystallises from alcohol in white needles and melts at 81—82° ; other products are also formed, but could not be isolated. The latter action is of interest, because it is the first observed by the authors in which a chlorine atom has been replaced by hydrogen under the influence of sodium ethoxide ; as a rule, the chlorine atom remains unaltered, or is replaced by an ethoxyl group, or, in the case of ethylic sodiomalonate or ethylic sodacetoacetate, by the radicles of these compounds (compare Jackson and Boos, Abstr., 1898, i, 517 ; Jackson and Soch, Abstr., 1896, i, 370 ; Dittrich, Abstr., 1890, 1418 ; Stieglitz, Abstr., 1891, 455, and Jackson and Lamar, Abstr., 1897, i, 29). W. A. D.

Comparative Study of the Three Dinitrobenzenes. By C. A. LOBRY DE BRUYN and ALPHONSE STEGER (*Rec. Trav. Chim.*, 1899, **18**, 9—12. Compare Abstr., 1894, i, 573).—An introduction to the succeeding paper. It is pointed out that in the case of the reaction there considered, the velocity is greatest for the para-, and least for the meta-compound ; this type of reaction is complementary to the two enumerated by Menschutkin (Abstr., 1898, 187). C. F. B.

Velocity of Substitution of a Nitro-group in Ortho- and Para-dinitrobenzene by Alkoxyl. By ALPHONSE STEGER (*Rec. Trav. Chim.*, 1899, 18, 13—40).—The velocity of the reaction was determined by dissolving a weighed quantity of dinitrobenzene in so much alcohol that the concentration of the former was about equal to that which it would have in the gaseous state, adding some alcoholic sodium alkoxide, usually the equivalent quantity, allowing the whole to remain at either 25°, 35°, or 45°, removing a portion at intervals, acidifying this with an excess of acetic acid, and titrating the excess of the latter. The reaction takes place according to the equation $NO_2 \cdot C_6H_4 \cdot NO_2 + NaOR = NO_2 \cdot C_6H_4 \cdot OR + NaNO_2$ [R = Me,Et] ; in the case of metadinitrobenzene, however, no such replacement occurs, reduction to dinitrazoxybenzene taking place instead. The co-efficient of velocity, k, was calculated by means of the equation $-dc/dt = kc^2$, where $c =$ the concentration, and the following values were obtained :

	Sodium Ethoxide.		Sodium Methoxide.	
	Ortho.	Para.	Ortho.	Para.
25°......	0·0260	0·211	0·0170	0·0442
35	0·0786	0·707	0·0484	0·143
45	0·233	2·21	0·139	0·474

The coefficient of increase of velocity with temperature, A, was also calculated by means of the equation $d\log_e k/dT = A/T^2$.

The rate of the reaction is greater with the para- than with the ortho-compound : 8·1—9·5 times as great with sodium ethoxide, 2·6—3·6 times with the methoxide. With sodium ethoxide, it is greater than with sodium methoxide : $1\frac{1}{2}$ times as great with the ortho-, 5 times with the para-compound ; this ratio is independent of the temperature. The temperature coefficient is in all cases about 2 ; rather greater for the para-, rather less for the ortho-compound. In the case of the ortho-compound, it was also found that the value of the constant is not affected by an excess of either reacting substance, or by dilution, or by the addition of a sodium salt (acetate or nitrite).

In the case of the analogous reaction, $CH_3I + NaOC_2H_5 = CH_3 \cdot OC_2H_5 + NaI$, it was found, on the other hand, that the constant increases slightly with the dilution, and is diminished slightly by the addition of sodium iodide. The latter result escaped the notice of Hecht, Conrad, and Brückner (*Abstr.*, 1890, 1046), because they operated with stronger solutions, in which the effect is less apparent.

C. F. B.

Influence of Water on the Velocity of Transformation of Orthodinitrobenzene by Sodium Methoxide and Ethoxide. By C. A. LOBRY DE BRUYN and ALPHONSE STEGER (*Rec. Trav. Chim.*, 1899, 18, 41—71).—The experiments were performed at 25° in the same way as when the pure alcohols were used as the solvents (preceding abstract), only, instead of these, the alcohols diluted with water in varying proportions were employed. Moreover, a certain quantity of nitrophenoxide is formed when dilute alcohol is employed, and this was estimated by a colorimetric method ; presumably, it results from the action on the dinitrobenzene of sodium hydroxide

formed by the action of the water on the alkoxide : $NO_2 \cdot C_6H_4 \cdot NO_2 + 2NaOH = NO_2 \cdot C_6H_4 \cdot ONa + NaNO_2 + H_2O$. As in the experiments with the pure alcohols, the velocity of transformation was found to be constant in each experiment ; the values of the constant are tabulated below, along with the amounts of sodium nitrophenoxide formed, expressed as mols. of nitrophenetoil or nitranisoil per mol. of sodium nitrophenoxide ; the strength of the alcohol is expressed as percentage by weight.

Strength of alcohol........		100	98	96	94	92	90	80	70	60.	50
Constant × 10⁴	Ethylic.	260	240	225	211	198	189	153	124	112	104
	Methylic.	169	172	—	—	—	182	197	209	225	249
Mols. alkoxy-compound per mol. phenoxide.	Ethylic.	∞	—	—	—	—	51	35	27	24·5	21
	Methylic.	∞	—	—	—	—	—	209	176	170	146

It will be seen that the addition of water diminishes the velocity of the reaction when ethylic alcohol is the solvent, increases it when the solvent is methylic alcohol. The amount of sodium phenoxide formed is always relatively small, and five times as small with the methylic as with the ethylic compound. In each experiment, the relation between the amounts of alkoxy-compound and phenoxide formed was found to remain constant throughout the experiment ; from this fact, the conclusion is drawn, after consideration of various alternatives, that the relation in question also expresses the relation between the amounts of sodium alkoxide and hydroxide present in the solution, from the action of which on the dinitrobenzene the alkoxy-compound and the phenoxide are formed respectively. If this be so, then a sodium alkoxide is by no means so easily decomposed by water (into alcohol and sodium hydroxide) as is commonly supposed, for the above table would then show that when sodium ethoxide is dissolved in ethylic alcohol diluted with an equal weight of water (the case where the greatest amount of decomposition was observed), only about 5 per cent. of it is so decomposed. No determinations of the constant of velocity could be made with more dilute alcohols, owing to the too small solubility therein of the dinitrobenzene ; experiments were made, however, in which the dinitrobenzene was boiled with the equivalent quantity of NaOH, dissolved in the dilute alcohol, until it had disappeared (8 or 16 hours), when the percentage that had been converted into alkoxy-compound was estimated, the rest having yielded phenoxide. The results were as follows :

Strength of Alcohol		40	20	10
Percentage converted	Ethylic	63	35	—
into alkoxy-compound	Methylic.........	96	88	70

Observations of other experimenters are cited in favour of the view that an alcoholic solution of sodium hydroxide contains alkoxide ; the authors themselves find that when sodium hydroxide is dissolved in

absolute ethylic or methylic alcohol, the same velocity constant is obtained in the reaction with dinitrobenzene as when the alkoxide is used instead of the hydroxide.

Some solubilities, at different temperatures, of ortho- and para-dinitrobenzene in ethylic and methylic alcohols of various strengths are recorded in the paper.　　　　　　　　　　　　　　　C. F. B.

Preparation of Mixed Ethylic and Phenylic Phosphates. By ALBERT MOREL (*Bull. Soc. Chim.*, 1899, [iii], **21**, 491—497. Compare this vol., i, 29, 264, 492).—These mixed phosphates are prepared by (i) the action of sodium ethoxide on the phenylic chlorophosphates; (ii) the action of sodium phenoxide on the ethylic chlorophosphates; (iii) the action of triphenylic phosphate on the alcohols and alkyloxides. By the action of alcohol on phenylic dichlorophosphate, *phenylic ethylic chlorophosphate*, OEt·PClO·OPh, is obtained; it is a colourless liquid which cannot be distilled; with water, it yields *phenylic ethylic phosphoric acid*, HO·PO(OEt)·OPh, as a colourless liquid. The *barium*, *lead*, and *sodium* salts are described.

Alcoholic ammonia reacts with phenylic ethylic chlorophosphate, yielding *phenylic ethylic phosphamide*, NH₂·PO(OEt)·OPh; it forms small, white crystals melting at 133°. Similarly, aniline yields *phenylic ethylic phosphanilide*, which crystallises from alcohol in white needles melting at 143°.　　　　　　　　　　　　　　　　　R. H. P.

Phenylic Chlorocarbonates. By ETIENNE BARRAL and ALBERT MOREL (*Compt. rend.*, 1899, **128**, 1578—1581).—Good yields of phenylic chlorocarbonates are obtained by the action of phosgene on the phenol in a sealed tube or on the aqueous sodium phenoxide. By this means, the chlorocarbonates from phenol, ortho- and para-cresols, guaiacol, thymol, trichlorophenol, tribromophenol, and pentachlorophenol have been prepared, the last two, however, giving only poor yields. In the case of α- and β-naphthols, the method fails, as the alkali naphthoxides are completely decomposed by phosgene and water into sodium carbonate and naphthol.　　　　　　　　　　　　　T. H. P.

Synthesis of Phenyltribromomethylcarbinol and its Reactions. By K. SIEGFRIED (*Chem. Centr.*, 1899, i, 606; from *J. Russ. Chem. Soc.*, 1898, **30**, 914—920).—*Phenyltribromomethylcarbinol*, prepared in a similar way to the chloro-compound by Jocitsch's method (*J. Russ. Chem. Soc.*, 1897, **29**, 97), crystallises from light petroleum in white needles, melts at 78—78·5°, is easily soluble in ether, soluble in light petroleum or hot water, and rather sparingly so in cold water. The *acetate* crystallises from benzene in large, refractive plates, melts at 140°, is easily soluble in alcohol, ether, or benzene, and soluble in light petroleum or cold water. The results of a crystallographic examination of the acetates of the chloro- and bromo-compounds by P. A. Semjatschensky are given in the original paper; both substances form monoclinic crystals. Although Jocitsch (*loc. cit.*) readily obtained phenylchloracetic acid by the action of potassium hydroxide solution on phenyltrichloromethylcarbinol, the bromo-compound, when treated with a 10 per cent. aqueous solution of potassium hydroxide, yields benzaldehyde, bromoform, and mandelic acid, only a very small

quantity of phenylbromacetic acid, mixed with a little mandelic acid, being formed when the process is carried out with great care.

When phenyltribromomethylcarbinol is distilled under 25 mm. pressure, and the temperature rises above 110°, hydrogen bromide is liberated, and dibromacetophenone, together with some bye-products, are formed. E. W. W.

Action of Zinc Dust on Alcoholic Solutions of α-Halogen-substituted Alcohols, and of Zinc Shavings on Alcoholic Solutions of their Acetates. By ŽIVOIN JOCITSCH (*Chem. Centr.* 1899, i, 606—607 ; from *J. Russ. Chem. Soc.*, 1898, **30**, 920—924). —By boiling acetonechloroform with alcohol and zinc dust, isobutylene is liberated, and the oil obtained by treating the product with water yields isocrotylic chloride boiling at 67—69° and dichlorisobutylene boiling at 107—109°. When phenyltrichloromethylcarbinol is similarly treated, two main fractions are obtained. The one, a colourless liquid of a pleasant odour, boils at 144—145°, and contains styrene, as, when treated with bromine, it forms a crystalline compound which melts at 75°. The second fraction boils at 195—197°, and is chlorostyrene. Phenyltribromomethylcarbinol, under similar conditions, yields styrene and bromostyrene. The reaction with zinc dust takes place in three stages, the first consisting in the removal of the elements of hypochlorous or hypobromous acid, and the second and third in the reduction of the di-halogenised, unsaturated hydrocarbon so formed, with liberation of hydrogen bromide. The elimination of the elements of hypochlorous or hypobromous acid is probably effected by the formation of intermediate organo-zinc compounds, which react with water in a similar way to the zinc alkyls. E. W. W.

Retardation of Chemical Reactions due to Stereochemical Influences. II. Hydroxybenzylic Bases. By CARL PAAL and FRIEDR. HÄRTEL (*Ber.*, 1899, **32**, 2057—2062. Compare this vol., i, 587).—The authors have studied the action of acetic anhydride on the three isomeric orthohydroxybenzylnitranilines prepared by the condensation of saligenin with the three nitranilines (compare Paal and Senninger, Abstr., 1894, i, 450). Orthohydroxyorthonitraniline is acted on by acetic anhydride only when the two are boiled together for some time, and the product formed is a monacetyl derivative, orthacetoxybenzylorthonitraniline. Orthohydroxybenzylmetanitraniline and the corresponding para-compound, when boiled with acetic anhydride, both yield diacetyl derivatives ; with the meta-compound, it is necessary to boil the mixture for some time, as otherwise a monacetyl derivative, orthohydroxymetanitracetanilide, is formed.

Orthohydroxybenzylorthonitraniline, $OH \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot NO_2$, crystallises in dark red plates or flat needles, melts at 125°, is readily soluble in acetone, chloroform, or benzene, and also in alkalis ; its *sodium* derivative is thrown down as a red, crystalline precipitate on the addition of concentrated sodium hydroxide. *Orthacetoxybenzyl-orthonitraniline* crystallises in yellow needles melting at 93°, and is soluble in ether, but not in light petroleum, or cold alkalis. *Orthohydroxymetanitraniline* crystallises from alcohol in glistening,

yellow needles melting at 115°. *Orthohydroxybenzylmetanitracetanilide,* $OH \cdot C_6H_4 \cdot CH_2 \cdot NAc \cdot C_6H_4 \cdot NO_2$, crystallises in nearly colourless prisms melting at 126°, and is readily soluble in alcohol, benzene, chloroform, or alkalis. *Orthacetoxybenzylmetanitracetanilide* crystallises in colourless, compact, concentrically arranged needles melting at 99°, and is readily soluble in alcohol, chloroform, or benzene, but insoluble in alkalis. *Orthohydroxybenzylparanitraniline* can only be obtained in small quantities by heating together an intimate mixture of the two constituents for 10—15 minutes at 150—160°; it crystallises in golden, glistening plates melting at 138°, and is readily soluble in most solvents with the exception of light petroleum. *Orthacetoxybenzylparanitracetanilide* crystallises in colourless needles melting at 79°; a monacetyl derivative could not be obtained.

Orthohydroxybenzylacetanilide, $OH \cdot C_6H_4 \cdot CH_2 \cdot NAcPh$, crystallises in colourless needles melting at 132°. *Orthacetoxybenzylacetanilide,* $OAc \cdot C_6H_4 \cdot CH_2 \cdot NAcPh$, crystallises in long, colourless plates melting at 98—99°. J. J. S.

Trimethylenimine. By Curtis C. Howard and Wilhelm Marckwald (*Ber.*, 1899, **32**, 2031—2035. Compare Gabriel and Weiner, Abstr., 1888, 1292; Ladenburg and Sieber, Abstr., 1890, 1394).— Trimethylenimine can be prepared in quantity and in a pure state by the action of sodium on a solution of paratoluenesulphotrimethylenimide, $C_6H_4Me \cdot SO_2 \cdot N{<}^{CH_2}_{CH_2}{>}CH_2$. It boils at 63° under 748 mm. pressure, fumes in the air, smells of ammonia, and has a sp. gr. 0·8436 at 20·4°. The base is unstable in presence of acids, and when warmed with dilute hydrochloric acid is converted into γ-chloropropylamine and its decomposition products. *Unsymmetrical trimethylenecarbamide,* $NH_2 \cdot CO \cdot NC_3H_6$, prepared by the action of cyanic acid on the base, crystallises in tablets, dissolves readily in water and slightly in alcohol, but not in ether, and melts at 207°. *Trimethylenimine trimethylenethiocarbamate,* $C_3H_6N \cdot CS \cdot SH, NC_3H_6$, prepared by the action of carbon bisulphide on an ethereal solution of the base, separates in white crystals, dissolves readily in alcohol, and slightly in benzene, but not in ether, and melts at 89°. *Trimethylenephenylthiocarbamide,* $NHPh \cdot CS \cdot NC_3H_6$, prepared by the action of phenylthiocyanate on the base, dissolves readily in alcohol or benzene and slightly in light petroleum, and melts at 110°. *Benzenesulphotrimethylenimide,* $C_6H_5 \cdot SO_2 \cdot NC_3H_6$, dissolves slightly in water or light petroleum in the cold, but readily in alcohol or benzene, and melts at 68°. *Nitrosotrimethylenimine,* $NO \cdot NC_3H_6$, is a pale yellow, oily liquid, miscible with water, and boils at 196—197°. T. M. L.

Constitution of Vinylamine. By Curtis C. Howard and Wilhelm Marckwald (*Ber.*, 1899, **32**, 2036—2038).—*Benzenesulphodimethylenimide,* $C_6H_5 \cdot SO_2 \cdot NC_3H_6$, prepared by the action of benzenesulphonic chloride on dimethylenimide (vinylamine), is a colourless, heavy oil insoluble in alkalis. *Paratoluenesulphodimethylenimide,* $C_6H_4Me \cdot SO_2 \cdot NC_3H_6$, crystallises from light petroleum, dissolves readily in alcohol, but only slightly in water, and melts at 52°.

The formation of these compounds proves the base to be secondary and not primary, and it must therefore be regarded as dimethylenimine, $NH<^{CH_2}_{CH_2}$, and not as vinylamine, $CH_2:CH\cdot NH_2$. This conclusion is confirmed by a comparison of the boiling points of the series,

		Diff.
Dimethylenimine	55—56° (756 mm.)	} 7·5°
Trimethylenimine......	63 (748 mm.)	} 25
Pyrrolidine	87·5—88·5	} 18
Piperidine.............	105—107	

the differences among the polymethylenecarboxylic acids being 8°, 23·5°, and 18·5° for the first four members of the series.   T. M. L.

Bistrimethylendi-imine. By CURTIS C. HOWARD and WILHELM MARCKWALD (*Ber.*, 1899, 32, 2038—2042).—The bistrimethylenedi-paratoluenesulphonimide, $C_7H_7\cdot SO_2\cdot N<^{C_3H_6}_{C_3H_6}>N\cdot SO_2C_7H_7$, recently described (this vol., i, 289), can be prepared by the action of trimethylenic bromide on the sodium salt of *diparatoluenesulphotrimethylendiamide*, $C_3H_6(NH\cdot SO_2\cdot C_7H_7)_2$; this substance dissolves readily in hot alcohol or benzene, and melts at 148°. *Bistrimethylendi-imine*, $NH<^{C_3H_6}_{C_3H_6}>NH$, prepared from the toluenesulphonic acid derivative by hydrolysis with 25 per cent. hydrochloric acid, is a thick, colourless liquid which boils at 186—188°, has a faint ammoniacal odour, fumes in the air, and solidifies in ice to a crystalline mass which melts at 14—15°. The *platinochloride*, $C_6H_{14}N_2,H_2PtCl_6$, melts with decomposition at 259°; the *aurichloride*, $C_6H_{14}N_2,2HAuCl_4$, melts at 216°; the *picrate*, $C_6H_{14}N_2,2C_6H_3N_3O_7$, forms long, slender needles and melts and decomposes at 226°. *Bistrimethylenedibenzimide* forms white crystals which are insoluble in water, but dissolve readily in hot alcohol or benzene, and melt at 124°.

Ethylenediparatoluenesulphonamide, $C_2H_4(NH\cdot SO_2\cdot C_7H_7)_2$, crystallises from acetic acid, dissolves readily in hot alcohol or benzene, and melts at 159·5—160·5°. *Trimethylenethylenediparatoluenesulphonimide*, $C_7H_7\cdot SO_2\cdot N<^{C_2H_4}_{C_3H_6}>N\cdot SO_2\cdot C_7H_7$, crystallises from absolute alcohol, dissolves readily in hot benzene or acetic acid, and melts at 150—151°. Trimethylenethylenedi-imine (compare Bleier, this vol., i, 664) melts at 42° and boils at 167° under 764 mm. pressure.   T. M. L.

History of Diazonium Salts. By EUGEN BAMBERGER (*Ber.*, 1899, 32, 2043—2046).—A reply to Hantzsch (this vol., i, 685). It is pointed out that not a single chemist used the Blomstrand diazonium formula until 1894, when the author brought forward reasons for accepting it, based mainly on the physical properties of the salts (Abstr., 1895, i, 134, 215, and 274). Hantzsch's physico-chemical researches on these compounds merely confirm what was previously known regarding them, and introduce no new factors.   J. J. S.

Orthodinitroso-derivatives of the Benzene Series. By Theodor Zincke and Ph. Schwarz (*Annalen*, 1899, 307, 28—49. Compare Abstr., 1896, i, 429).—This paper contains experimental details relating to the summary which has already appeared (*loc. cit.*).

Phenylenefurazan, $C_6H_4 \ll_N^N \!\!> O$, the anhydride of benzeneorthodioxime, is obtained when the latter is distilled with dilute caustic soda; it crystallises from alcohol in long, white needles, and melts at 55°.

1 : 3 : 4-*Nitrotolylhydrazine* crystallises from hot water in deep red needles and melts at 110—111°; the hydrochloride forms golden-yellow leaflets.

Nitrodiazotolueneimide [Me : NO_2 : $N_3 = 1 : 3 : 4$], prepared by the action of nitrous acid, crystallises from benzene in long needles or thickened plates, and melts at 35°; at the temperature of the water-bath, it is converted into orthodinitrosotoluene [Me : $(NO)_2 = 1 : 3 : 4$].

Toluenedioxime [Me : $(NOH)_2 = 1 : 3 : 4$] crystallises from hot water in small, yellowish-brown needles, and melts at 127—128°; 1 : 3 : 4-*tolylenefurazan* is very volatile, and crystallises from dilute alcohol in long, white needles melting at 37°.

Nitrodiazotolueneimide [Me : N_3 : $NO_2 = 1 : 2 : 3$], prepared by the action of ammonia on the diazoperbromide derived from 1 : 2 : 3-nitrotoluidine, crystallises from alcohol and melts at 50°. *Toluenedioxime* [Me : $(NOH)_2 = 1 : 2 : 3$] melts and decomposes at 140°, and when distilled with aqueous alkali, yields 1 : 2 : 3-*tolylenefurazan*, which melts at 44°.

Nitrodiazometaxyleneimide [Me_2 : N_3 : $NO_2 = 1 : 3 : 4 : 5$] melts at 66° *Metaxylenedioxime* [Me_2 : $(NOH)_2 = 1 : 3 : 4 : 5$] melts and decomposes at 142°; elimination of water gives rise to 1 : 3 : 4 : 5-*metaxylylenefurazan*, which crystallises from dilute alcohol in long, white needles, and melts at 60°. M. O. F.

Nitro-derivatives of Orthodinitrosobenzene. By P. Drost (*Annalen*, 1899, 307, 49—69).—*Orthonitrorthodinitrosobenzene* [NO_2 : $(NO)_2 = 1 : 2 : 3$], obtained from orthodinitrosobenzene and nitric acid when excess of the latter is avoided, crystallises from glacial acetic acid in thin, yellow leaflets, and melts at 143°.

Fuming nitric acid converts it into *metadinitrorthodinitrosobenzene* [$(NO_2)_2$: $(NO)_2 = 1 : 3 : 4 : 5$], which crystallises in yellow needles and melts at 172°; the *potassium* derivative forms lustrous, golden leaflets, containing $\frac{1}{2}H_2O$, and the *sodium*, *silver*, and *ammonium* derivatives are well-defined. The additive *compound* with naphthalene crystallises from alcohol in long, red needles, and melts and decomposes at 172°. The *anilide*, $NHPh \cdot C_6H(NO_2)_2(NOH)_2$, obtained by heating dinitrodinitrosobenzene with aniline in alcohol, forms a red, crystalline powder, which blackens and detonates when heated; the *potassium* and *ammonium* derivatives yield red crystals, and the *aniline* compound forms a reddish-brown powder, which detonates when heated. When metadinitrorthodinitrosobenzene is reduced with tin and hydrochloric acid at common temperatures, 1 : 2 : 3 : 5-tetramidobenzene is obtained.

Dinitrodiazobenzeneimide [$(NO_2)_2$: $N_3 = 1 : 3 : 4$], prepared by the

action of ammonia on the diazoperbromide derived from dinitraniline, and by nitrating orthonitrobenzenediazoimide or paranitrobenzene-diazoimide, crystallises from dilute acetic acid in pale yellow needles melting at 69°. *Paranitrorthodinitrosobenzene* $[NO_2 : (NO)_2 = 1 : 3 : 4]$, obtained by heating the dinitro-imide on a water-bath, crystallises from a mixture of benzene and light petroleum in plates which contain benzene ; it melts at 72°.

Symmetrical orthodinitrorthodinitrosobenzene $[(NO_2)_2 : (NO)_2 = 1 : 2 : 4 : 5]$, produced on dissolving paranitrorthodinitrosobenzene in fuming nitric acid, separates from nitric acid of sp. gr. 1·4 in small, pale yellow crystals which melt at 172°, evolving brown gas ; the *dianilide* forms dark red, slender needles, and melts at 168°. Symmetrical tetramidobenzene is obtained on reducing the dinitro-dinitroso-derivative with tin and hydrochloric acid.

Orthonitrophenylenefurazan, $NO_2 \cdot C_6H_3 \underset{N}{\overset{N}{\lessgtr}} O$, prepared from phenylenefurazan and fuming nitric acid, forms small, pale yellow crystals, and melts at 98° ; reduction with tin and hydrochloric acid converts it into 1 : 2 : 3-triamidobenzene. M. O. F.

Combination of Phenylhydrazine and other Bases with Metallic Salts. By JOSEPH MOITESSIER (*Compt. rend.*, 1899, **128**, 1336—1337).—Compounds of metallic salts with phenylhydrazine and other bases can be obtained by mixing saturated alcoholic solutions of the proximate constituents in the proper proportions. As a rule, the compounds crystallise well, and are only slightly soluble in water or alcohol. The compound $ZnI_2, NH_2Ph, 2N_2H_3Ph$ forms needles which melt at 180°, and rapidly decompose at a slightly higher temperature ; they are soluble in ether or alcohol. The compound

$$3ZnBr_2, 5NH_2Ph, 2N_2H_3Ph,$$
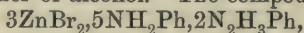
forms long, silky, curved needles ; the compound $NiSO_4, NH_2Ph, 2N_2H_3Ph + 2H_2O$ is a greenish-white, crystalline powder insoluble in ether ; the compound $2Cd(NO_3)_2, 3NH_2Ph, 5N_2H_3Ph$ melts and decomposes at 195°, and is insoluble in ether ; the compound $ZnI_2, C_{10}H_7 \cdot NH_2, 2N_2H_3Ph$ forms long, prismatic needles which melt and decompose at 115°, and are soluble in ether or alcohol, whilst the corresponding β-naphthyl-amine compound, $3ZnI_2, 2C_{10}H_7 \cdot NH_2, 4N_2H_3Ph$, decomposes at 155°, and is soluble in ether or alcohol, but only slightly soluble in benzene or chloroform.

If any of these compounds is treated with excess of Fehling's solution, the phenylhydrazine is decomposed and the other organic base is liberated, and can be extracted with ether (compare Abstr., 1898, i, 132, 133, and 413). C. H. B.

New Coloured Phenylhydrazones. By MARIUS ROUGY (*Bull. Soc. Chim.*, 1899, [iii], **21**, 593—597).—*Orthonitrobenzaldehyde meta-nitrophenylhydrazone*, $NO_2 \cdot C_6H_4 \cdot CH:N_2H \cdot C_6H_4 \cdot NO_2$, prepared by heating in alcoholic solution molecular proportions of metanitrophenyl-hydrazine and orthonitrobenzaldehyde, separates from alcohol in small, red crystals melting at 203°, and is soluble in benzene or ether, but insoluble in light petroleum.
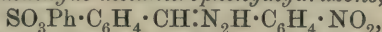
Metanitrobenzaldehyde metanitrophenylhydrazone separates from

alcohol in small, maroon crystals melting at 209°, and dissolves in ether or benzene, but is insoluble in light petroleum.
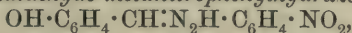
Paranitrobenzaldehyde metanitrophenylhydrazone separates from alcohol in small, red crystals melting at 216°, and is soluble in ether or benzene, but insoluble in light petroleum.

Orthosulphobenzaldehyde metanitrophenylhydrazone,

$$SO_3Ph \cdot C_6H_4 \cdot CH:N_2H \cdot C_6H_4 \cdot NO_2,$$

obtained by the interaction at ordinary temperatures of molecular proportions of an 8 per cent. solution of sodium orthobenzaldehyde-sulphonate and a solution of metanitrophenylhydrazine made faintly acid with acetic acid, separates from alcohol in orange-yellow crystals which dye wool orange-yellow.

Orthohydroxybenzaldehyde metanitrophenylhydrazone,

$$OH \cdot C_6H_4 \cdot CH:N_2H \cdot C_6H_4 \cdot NO_2,$$

forms small, maroon crystals melting at 76°, and is soluble in alcohol, ether, or benzene, but insoluble in light petroleum.

Metanitracetophenone phenylhydrazone, $NO_2 \cdot C_6H_4 \cdot CMe:N_2HPh,$ separates from alcohol in small, orange crystals melting at 126°, and is soluble in alcohol, ether, or benzene, but insoluble in light petroleum.

Metanitracetophenone orthosulphophenylhydrazone,

$$NO_2 \cdot C_6H_4 \cdot CMe:N_2H \cdot C_6H_4 \cdot SO_3H,$$
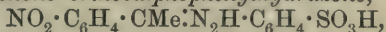
forms small, yellow crystals, and, in acid solution, dyes wool a beautiful yellow, resembling that given by auramine.

Metanitrophenylpyrazolone, $NO_2 \cdot C_6H_4 \cdot N{<}^{N\,:\,CMe}_{CO \cdot CH_2}$, prepared by the interaction of molecular proportions of metanitrophenylhydrazine and ethylic acetoacetate, separates from alcohol in beautiful, maroon crystals melting at 119°, and is soluble in ether or benzene, but insoluble in light petroleum.   T. H. P.

Orthochlorobenzhydroximic Chloride and its Derivatives. By ALFRED WERNER and C. BLOCH (*Ber.*, 1899, **32**, 1975—1985. Compare this vol., i, 690).—*Orthochlorobenzaldoxime* separates from alcohol in thick needles, and from water in thread-like crystals, and melts at 75—76°. *Orthochlorobenzhydroximic chloride,* $C_6H_4Cl \cdot CCl:NOH$, was obtained as a thick oil which could not be distilled, but occasionally deposited crystals melting at 55—56°; the oil appears to be a mixture of the two stereoisomerides. *Orthochlorobenzenylamidoxime,* $C_6H_4Cl \cdot C(NH_2):NOH$, melts at 117°, crystallises from hot water in needles, and from alcohol in stout prisms, dissolves readily in ether, benzene, light petroleum, or acetic acid, as well as in acids or caustic alkalis; the *hydrochloride* crystallises in small needles, melts at 225°, and dissolves readily in water or alcohol, but not in other organic solvents; the *nitrate* separates from the aqueous solution in small needles and melts at 237°. The *benzoate* crystallises from hot alcohol in needles and melts at 162°; it is soluble in dilute acids, but not in water or alkalis, and dissolves readily in ether, alcohol, or acetic acid, but only slightly in light petroleum or benzene. On fusing the benzoate or boiling its alcoholic solution, it gradually loses water, and is converted into *orthochlorobenzenylazoxime,* $C_6H_4Cl \cdot C{<}^{N\,:\,CPh}_{N\!-\!O}{>}$; this

crystallises in white needles, melts at 165°, and dissolves readily in ether or acetic acid, but only slightly in benzene, light petroleum, or alcohol. *Orthochlorobenzenylanilidoxime*, $C_6H_4Cl·C(NHPh):NOH$, crystallises from dilute alcohol in silky needles, melts at 140°, dissolves in acids or alkalis, and is readily soluble in ether or alcohol, but only slightly in water, light petroleum, or acetic acid. *Orthochlorobenzenyltoluidoxime*, $C_6H_4Cl·C(NH·C_6H_4Me):NOH$, crystallises from alcohol in needles and melts at 173°. *Orthochlorobenzenylpiperidoxime*, $C_6H_4Cl·C(C_5NH_{10}):NOH$, crystallises in well-formed, glistening rhombohedra and melts at 165°. *Orthodichlorodibenzenylazoxime*,

$$C_6H_4Cl \diagdown \begin{matrix} N:C·C_6H_4Cl \\ N·O \end{matrix}$$

, is produced by heating orthochlorobenzhydroximic chloride until the evolution of gas ceases; it crystallises from dilute alcohol in thread-like needles and melts at 93°. *Dichlorobenzildioxime peroxide*, $\begin{matrix} C_6H_4Cl·C:N·O \\ C_6H_4Cl·C:N·O \end{matrix}$, is produced, together with a certain amount of orthochlorobenzhydroxamic acid, on heating orthochlorobenzhydroximic chloride with dilute sodium hydroxide; it melts at 131°, crystallises from alcohol in needles, does not dissolve in acids or alkalis, or in water or light petroleum, but dissolves slightly in benzene and readily in ether, alcohol, or acetic acid. On reduction with zinc dust and acetic acid, it gives *orthodichlorobenzilsyndioxime*, $C_2(NOH)_2(C_6H_4Cl)_2$; this crystallises from alcohol in needles and melts at 226—227°, dissolves readily in dilute alkalis, and in ether, alcohol, or benzene, but only slightly in light petroleum or acetic acid, and is insoluble in water. The *diacetate* crystallises in slender needles, melts at 129°, dissolves readily in alcohol or ether, and slightly in benzene; the *dipropionate* melts at 97°, and resembles the acetate; by heating with caustic potash, both are converted into

diorthochlorophenylfurazan, $O \diagdown \begin{matrix} N:C·C_6H_4Cl \\ N:C·C_6H_4Cl' \end{matrix}$ which crystallises from alcohol in prisms, melts at 107°, and is insoluble in water, acids, or alkalis, but dissolves slightly in light petroleum and readily in ether, alcohol, acetic acid, or benzene. *Orthodichlorobenzilantidioxime* is produced on boiling an alcoholic solution of the syndioxime; it crystallises from benzene in microscopic needles, melts at 270°, dissolves readily in dilute alkalis and in ether or acetic acid, is slightly soluble in benzene, alcohol, or light petroleum, and insoluble in water. The *diacetate* melts at 157°, dissolves readily in alcohol or ether, slightly in benzene, and not at all in water, acetic acid, or light petroleum; the *dipropionate* crystallises from alcohol in colourless needles and melts at 105°; both compounds are hydrolysed by dilute alkalis, giving back the antidioxime and not the furazan derivative.

                                                            T. M. L.

Behaviour of Acetanilide in Solutions of Zinc Chloride and Hydrogen Peroxide. By W. Bräutigam (*Chem. Centr.*, 1899, i, 560; from *Pharm. Zeit.*, 44, 75).—By the action of zinc chloride on acetanilide at 180°, the yellow dye flavaniline is formed, but acetanilide is not attacked by boiling with zinc chloride in aqueous solution or with hydrogen peroxide. By boiling an aqueous solution with

hydrogen peroxide and zinc chloride, however, a carmine red liquid is formed which, on further heating, becomes brownish-red and on cooling deposits a brownish-red powder which is insoluble in ether. This reaction is characteristic of acetanilide, for under similar conditions phenacetin gives only a yellowish coloration and antipyrine a yellowish precipitate.　　　　　　　　　　　　　　　　　　　E. W. W.

Derivatives of Metamidophenol. By RICHARD E. MEYER and W. SUNDMACHER (*Ber.*, 1899, **32**, 2112—2124. Compare Abstr., 1878, 237 ; Ikuta, *ibid.*, 1893, i, 265).—A yield of some 70 per cent. of metamidophenol may be obtained by fusing metamidobenzenesulphonic acid with sodium hydroxide (Germ. pat. 44792) ; it melts at 121—122° (Ikuta gives 122—123°) and readily forms azo-dyes.

Metahydroxyphenylcarbamide, $OH \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, obtained by mixing concentrated aqueous solutions of potassium cyanate and of metamidophenol hydrochloride, crystallises from boiling water in large, colourless prisms melting at 180—181° and readily soluble in alcohol, acetone, or acetic acid, but practically insoluble in benzene or light petroleum. When the carbamide is heated with aniline at 180—190°, ammonia is evolved and *metahydroxycarbanilide*, $OH \cdot C_6H_4 \cdot NH \cdot CO \cdot NHPh$, is formed ; this crystallises in glistening, felted needles melting at 230—232°, and is only sparingly soluble in hot water. Metadihydroxycarbanilide (compare Struve and Radenhausen, Abstr., 1896, i, 35) is obtained when metahydroxyphenylcarbamide and metamidophenol are heated at 180—190°.

Metahydroxyphenylthiocarbamide, $OH \cdot C_6H_4 \cdot NH \cdot CS \cdot NH_2$, crystallises from water in large, colourless prisms melting at 183—184°.

Metahydroxythiocarbanilide, $OH \cdot C_6H_4 \cdot NH \cdot CS \cdot NHPh$, is obtained when an alcoholic solution of metamidophenol and phenylthiocarbimide is warmed on the water-bath for an hour and then allowed to remain for a day ; it crystallises in glistening, pearly plates melting at 155—156°. *Metadihydroxythiocarbanilide*, $CS(NH \cdot C_6H_4 \cdot OH)_2$, is formed when the amidophenol is boiled for about 15 hours with an alcoholic solution of rather more than the theoretical amount of carbon bisulphide ; it crystallises from water in pale yellow needles melting at 164—165°, and is readily soluble in most organic solvents with the exception of benzene and light petroleum.

Ethylic metahydroxyphenyloxamate, $OH \cdot C_6H_4 \cdot NH \cdot CO \cdot COOEt$, obtained in the same manner as the ortho- and para-compounds (Abstr., 1896, i, 367 ; 1898, i, 320), crystallises in thick, colourless needles melting at 183—184° ; it is readily hydrolysed by warm dilute sodium hydroxide ; the *acid* forms colourless, compact crystals melting and decomposing at 215°. *Metahydroxyphenyloxamide*,
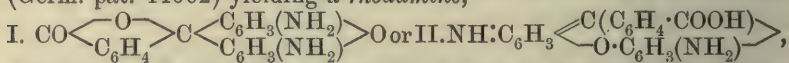
$$OH \cdot C_6H_4 \cdot NH \cdot CO \cdot CONH_2,$$

crystallises in glistening needles melting at 225—227° and is readily soluble in alkalis.

Metadihydroxydiphenyloxamide, $C_2O_2(NH \cdot C_6H_4 \cdot OH)_2$, obtained by heating a mixture of ethylic oxalate and metamidophenol at 170° for half an hour, crystallises in colourless, glistening plates melting at 269—270°.

Phthalic anhydride can condense with either one or two molecular

proportions of alkylated metamidophenols, yielding respectively alkyl derivatives of metamidohydroxybenzoylbenzoic acid (Germ. pat. 85931) and rhodamines. Metamidophenol itself readily condenses with phthalic anhydride in the presence of concentrated sulphuric acid (Germ. pat. 44002) yielding a *rhodamine*,

$$\text{I. } CO\diagdown\!$$

I. $CO\!<^{O}_{C_6H_4}\!>C\!<^{C_6H_3(NH_2)}_{C_6H_3(NH_2)}\!>O$ or II. $NH\!:\!C_6H_3\!<^{C(C_6H_4\cdot COOH)}_{O\cdot C_6H_3(NH_2)}\!>$,

which is isomeric with 2 : 7-diamidofluoran and with *i*-diamidofluoran (Meyer and Friedland, Abstr., 1898, i, 590). It crystallises in reddish-brown plates, begins to sinter at 230°, and melts at 250—252°, dissolves readily in methylic, ethylic, or amylic alcohol, in acetone or acetic acid, yielding reddish-yellow solutions with an intense green fluorescence, but is only sparingly soluble in benzene or ether, yielding colourless, non-fluorescent solutions; it is insoluble in light petroleum, but dissolves readily in mineral acids, and may be precipitated from such solutions on the addition of not too large a quantity of alkali. The *hydrochloride*, $C_{20}H_{14}N_2O_3,HCl$, with the quinonoid structure II, crystallises in reddish-brown plates with a green metallic lustre; the *sulphate*, $C_{20}H_{14}N_2O_3,H_2SO_4$, crystallises in large, lustrous, green needles, and the *acetyl* derivative in yellow plates melting at 170—173°. When dissolved in hot dilute sulphuric acid and treated while still hot with sodium nitrite, rhodamine is converted into fluorescein.

Molecular proportions of metamidophenol and of phthalic anhydride in hot toluene condense in quite a different manner from alkylated metamidophenols and the same anhydride (*loc. cit.*), the product formed being *metahydroxyphthalamic acid*, $OH\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot COOH$, which crystallises in minute, felted needles, melting at 227—229°, and fairly readily soluble in alcohol, ether, or acetic acid.

Most primary amines, when mixed with an acid anhydride, in molecular proportion and in the presence of an indifferent solvent, react in the same manner, the amido-group taking part in the condensation. Phthalic anhydride and aniline in toluene solution yield phthalanilic acid melting at 170°, with conversion into phthalanil, which then melts at 203° (Laurent and Gerhardt give 192°, Zincke 158°, and Thorp 191—193° as the melting point of the anilic acid). Benzoic anhydride and aniline, under similar conditions, yield benzoic acid and benzanilide; the same anhydride and metamidophenol yield benzoic acid and meta-hydroxybenzanilide (compare Ikuta, *loc. cit.*). J. J. S.

Aromatic Carbimides. By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 586—593).—The authors have discovered a new method of preparing aromatic carbimides by which good yields of the pure products are readily obtained. This consists in treating a solution of the aromatic base in benzene with a solution of phosgene in toluene; one mol. of the carbimide is first formed along with two mols. of the hydrochloride of the base, and then, by prolonged heating in presence of excess of phosgene, this hydrochloride is converted into the carbimide. Thus by the action of phosgene on the nitranilines, 2-, 3-, and 4-nitrophenylcarbimides have been prepared, and from them the corresponding ethylic nitrophenylcarbamates.

Metanitroparatolylcarbimide, obtained by the action of excess of phosgene on metanitroparatoluidine, forms small, yellow needles melting at 57—58°, and is soluble in benzene, toluene, chloroform, or ether, but only dissolves slightly in cold light petroleum, although more so on heating.

Ethylic metanitroparatolylcarbamate, $[\text{Me}:\text{NO}_2:\text{NH}\cdot\text{COOEt} = 1:3:4]$, formed by the interaction of alcohol and the corresponding nitrocarbimide, in molecular proportion, crystallises from 95 per cent. alcohol in beautiful, amber-yellow, prismatic needles melting at 63°; it is very soluble in benzene or ether, less so in light petroleum, and is insoluble in water in the cold, but dissolves appreciably on heating.

5·*Nitrorthotolylcarbimide*, $[\text{Me}:\text{NO}_2:\text{NCO} = 1:5:2]$, obtained from 5-nitrorthotoluidine, crystallises in light yellow, microscopic needles melting at 127°, and is soluble in benzene, toluene, ether, chloroform, or light petroleum.

Ethylic 5-nitrorthotolylcarbamate $[\text{Me}:\text{NH}\cdot\text{COOEt}:\text{NO}_2 = 1:2:5]$ crystallises from alcohol in pale yellow needles melting at 127°, and is soluble in benzene, ether, or water, but almost insoluble in light petroleum.

Paranitrorthotolylcarbimide, prepared from metanitrorthotoluidine, crystallises in small, white needles melting at 48—49°, and is soluble in benzene, toluene, ether, chloroform, or light petroleum.

Ethylic paranitrorthotolylcarbamate crystallises from alcohol in thin, white needles melting at 129—130°, and readily dissolves in benzene or ether, but is less soluble in light petroleum or water.

Orthonitroparatolylcarbimide, prepared from orthonitroparatoluidine, forms white prisms melting at 49—50°, and is soluble in benzene, toluene, ether, chloroform, or light petroleum.

Ethylic orthonitroparatolylcarbamate separates from aqueous alcohol in the form of microscopic, pale yellow needles melting at 77—78°, fairly soluble in benzene or boiling water, less so in ether, and insoluble in light petroleum or cold water.

All these nitrotolylcarbamides are decomposed by the prolonged action of boiling water, carbonic anhydride being evolved and the corresponding carbamide and fundamental base formed.　　　T. H. P.

Nitration of Benzoic Acid and of its Methylic and Ethylic Salts. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1899, **18**, 267—291).—The acid or ethereal salt (3 grams) was introduced in successive small quantities into five times the weight of pure nitric acid, the temperature of the latter being maintained constant within 5°; the solution was allowed to remain for a quarter of an hour, and then poured into iced water (120 c.c.). In the case of the acids, the precipitate was filtered off, and the substance dissolved in the filtrate was recovered by extraction with ether; in the case of the alkylic salts, the product was extracted at once with ether, and hydrolysed by warming with normal alkali, the acids being afterwards extracted with ether. The yield was nearly equal to that calculated on the assumption that mononitro-products only were formed. The

proportions in which the meta-, ortho-, and para-isomerides were
present in the product were determined by a method which is
an improvement on that previously described (this vol., ii, 257).
In order to estimate the amount of para-compound present, a weighed
quantity of the product was shaken in a bottle at $24\cdot4°$ with excess of
the pure meta- and ortho-acid, and about 65 c.c. water; at the same
time, a mixture of the pure meta- and para-acids only was shaken with
water in the same way. From the first bottle, two portions of 25 c.c.
were removed by means of a pipette furnished with a plug of cotton
wool; pipette and plug were then rinsed back into the bottle with
about 50 c.c. of water. From the second bottle, 25 c.c. were removed,
and an equal amount of water added without special precaution; both
solutions were then shaken again. Of the liquid removed from each
bottle, 25 c.c. were titrated with $N/20$ baryta; both solutions were
saturated with meta- and ortho-acid, but that from the first bottle
contained para-acid in addition, and consequently required more
baryta; the difference in the amounts of baryta required multiplied
by 2, is equivalent to the amount of para-acid present in the 25×2 c.c.
of solution removed from the first bottle. The process is continued
until the solutions from both bottles require the same amount of
baryta; all the para-acid has then been removed from the first bottle.
The sum of the differences obtained in the successive pairs of titrations
is equivalent to the total weight of para-acid present in the weight of
the product operated on. In the case of the ortho- and meta-acids,
which are much more soluble in water, the solubility of the other two
acids was found to be affected by the amount of the ortho- or meta-acid
which had dissolved, with the result that the amount of ortho-acid found
came out too low, that of meta-acid too high; however, by making ex-
periments in which different weighed quantities of each pure acid
were shaken with excess of the other two acids in the manner de-
scribed above, and comparing the amount found with that taken, it
was possible to ascertain the correction to be applied to any quantity
found by the experiment. In the actual experiments, the amounts of
para- and ortho-compounds only were estimated as described; that of
the meta-compound was calculated by difference. In all cases, a
correction had to be applied for a small amount of acid impurity intro-
duced through the use of the ether; this was ascertained by shaking
simultaneously with water (1) some of the product along with excess
of pure meta-, ortho-, and para-acids, and (2) the mixture of the three
pure acids only, in the manner described above, and noting the
difference in the amounts of baryta solution required. In an experi-
ment made to test the method, it was found that the absolute error
in the determination of the amount of each isomeride was rather
less than 1 ($0\cdot2$—$0\cdot8$) per cent. of the weight of the product operated
upon.

The results of the determinations are recorded in the table; the
numbers express the percentage of each isomeride in the product of
nitration. The temperature of $-30°$ was obtained by means of a mix-
ture of solid carbonic anhydride and 95 per cent. alcohol contained
in a vessel jacketed with pure, dry wool.

Nitration at		$-30°\,(-40°$ for Ethylic benzoate)	$0°$	$+30°$
Benzoic acid	ortho	14·4	18·5	22·3
	meta	85·0	80·2	76·5
	para	0·6	1·3	1·2
Methylic benzoate	ortho	23·6	21·0	25·7
	meta	74·4	73·2	69·8
	para	2·0	5·8(?)	4·5
Ethylic benzoate	ortho	25·5	28·3	27·7
	meta	73·2	68·4	66·4
	para	1·3	3·3	5·9

It will be seen that in all cases the meta-compound remains the chief product of the nitration, but that the amount decreases as the temperature rises; in the case of benzoic acid itself, the amount of ortho-compound formed increases considerably with the temperature of nitration, whilst that of the para-compound increases but little; with its ethereal salts, the converse is the case. It appears further that, on the whole, successive substitution of the H of the COOH group by Me and Et occasions a gradual decrease of the amount of meta-compound formed and increase of the amounts of ortho- and para-compounds.

The formation of a para-derivative in the nitration of alkylic benzoates, unnoticed hitherto, was proved by isolating paranitro-benzoic acid from the product. C. F. B.

Camphoric Acid. VI. By WILLIAM A. NOYES (*Amer. Chem. J.,* 1899, **22**, 1—5. Compare this vol., i, 284).—1 : 3 : 2-*Hexahydro-xylic acid* [$Me_2 : CO_2H = 1 : 3 : 2$], prepared by reducing 2 : 6-dimethylbenzoic acid (*loc. cit.*) with sodium and amylic alcohol, crystallises from light petroleum or benzene, melts at 72°, boils at 250—252°, and is volatile with steam; on treatment with phosphorus pentachloride and bromine, it yields *a-bromohexahydro-xylic chloride,* which is not hydrolysed on boiling with water or 10 per cent. caustic soda, although it is readily decomposed when warmed with glacial formic acid, giving rise to *a-bromohexahydro-xylic acid,* $C_9H_{15}BrO_2$. This crystallises from formic acid in leaflets, melts at 150—151°, and, when warmed with alcoholic potash, yields Δ^1-*tetrahydro-xylic acid,* $C_9H_{14}O_2$, which separates from light petroleum in compact crystals, melts at 89—90°, and is only slowly oxidised by potassium permanganate.

The properties given for Δ^1-tetrahydro-xylic acid and the compounds from which it was obtained plainly indicate its non-identity with *cis*-campholytic acid; Collie's formula for camphoric acid (Abstr., 1892, 864) is therefore no longer admissible. W. A. D.

a-**Amido-acids.** By EMIL ERLENMEYER, jun. (*Annalen,* 1899, **307**, 70—113).—This paper comprises a theoretical discussion of the author's previous work on the *a*-amido-acids, and of the results described in the following abstracts.

In a former paper (Abstr., 1895, i, 281), the properties of phenyl-*a* amidolactic acid were recorded. Another modification has been isolated from among the products of condensation of benzaldehyde and glycocine under the influence of caustic soda; it crystallises in small, white needles on adding absolute alcohol to the concentrated aqueous

solution, and melts at 187—188°, instead of 196°. The new acid contains $1H_2O$, and dissolves in 17 parts of water instead of 38 parts ; the *copper* salt is pale blue, and dissolves in 255 parts of water instead of 2108 parts.

The relationship of the stereoisomeric diphenylhydroxyethylamines is considered at some length, and the following conclusions are drawn concerning the behaviour of amido-acids towards aldehydes. 1. The *a*-methylenic group in amidocarboxylic acids undergoes condensation with aldehydes in presence of caustic soda. 2. The methylenic group in benzylamine is capable of undergoing the same change. 3. The double linking in the complex $COOH \cdot CH \cdot N \vdots CH \cdot$ is capable of changing its position, giving rise to the group $COOH \cdot C \vdots N \cdot CH_2 \cdot$. 4. The complex $COOH \cdot C(OH) \cdot NH \cdot CH \cdot OH$ can change into the group $COOH \cdot CH \cdot NH \cdot CO$, as illustrated by the formation of phenylacetyl-phenylalanine from phenylpyruvic acid and ammonia.   M. O. F.

The Two Stereoisomeric Diphenylhydroxyethylamine Bases. By EMIL ERLENMEYER, jun. (*Annalen*, 1899, 307, 113—137. Compare Abstr., 1896, i, 305 ; 1897, i, 480, and foregoing abstract).—The *benzylidene* derivative of isodiphenylhydroxyethylamine,

$$OH \cdot CHPh \cdot CHPh \cdot N \vdots CHPh,$$
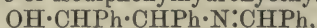
is prepared by exposing a mixture of glycocine dissolved in water, benzaldehyde in alcohol, and caustic soda in water, to direct sunlight during 10 hours, or to a temperature of 55° during 5 hours (compare Abstr., 1895, i, 596) ; it melts at 134°, and crystallises from alcohol in monoclinic needles [$a : b : c = 2 \cdot 22905 : 1 : 2 \cdot 1187$. $\beta = 82° \; 8'$]. The *acetyl* derivative crystallises from alcohol and melts at 117°.

Hydrochloric acid resolves the benzylidene derivative into benzaldehyde and isodiphenylhydroxyethylamine, which melts at 129—130°, and crystallises from methylic alcohol in monoclinic plates [$a : b : c = 3 \cdot 3339 : 1 : 2 \cdot 2396$. $\beta = 70° \; 15'$]. The hydrochloride melts and decomposes at 211° ; it crystallises from methylic alcohol in long, six-sided plates which contain 1 mol. of the solvent and belong to the triclinic system [$a : b : c = 0 \cdot 60151 : 1 : 1 \cdot 1631$. $a = 88° \; 42' ; \beta = 119° \; 40' ; \gamma = 90° \; 25'$].

Diphenylhydroxyethylamine is prepared according to the method of Goldschmidt and Polonowska by reducing benzoinoxime with sodium amalgam and glacial acetic acid (compare Söderbaum, Abstr., 1896, i, 98) ; it melts at 163°, and crystallises from alcohol in colourless, lustrous needles belonging to the monoclinic system [$a : b : c = 2 \cdot 1370 : 1 : 2 \cdot 8933$. $\beta = 74° \; 23'$]. The hydrochloride crystallises from methylic alcohol in needles belonging to the hexagonal system ; it contains 1 mol. of the solvent, and decomposes at 234°. When the base is heated at temperatures slightly above the melting point, it is resolved into benzylamine and benzaldehyde, a change which the isomeride also undergoes when submitted to similar conditions.   M. O. F.

Synthesis of Tyrosine. By EMIL ERLENMEYER, jun., and JOHN T. HALSEY (*Annalen*, 1899, 307, 138—145. Compare Abstr., 1899, 30, 197).—The *lactimide*, $OAc \cdot C_6H_4 \cdot CH \vdots C < \overset{N Bz}{\underset{CO}{|}}$, prepared by heating

parahydroxybenzaldehyde, hippuric acid, anhydrous sodium acetate, and acetic anhydride during 10—15 minutes on the water-bath, crystallises from dilute alcohol in small, yellow needles, and melts at 172—173°. *Parahydroxy-α-benzamidocinnamic acid*,

$$OH \cdot C_6H_4 \cdot C(NHBz) \colon CH \cdot COOH,$$
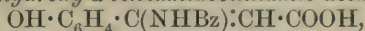
obtained on hydrolysing the lactimide with hot, aqueous, caustic soda, crystallises from dilute alcohol in white needles, and melts at 228—229°, when it decomposes; reduction with sodium amalgam in alkaline solution gives rise to benzoyltyrosine, which yields tyrosine under the influence of concentrated hydrochloric acid at 150°.　　　　　M. O. F.

Formation of Phenylacetylphenylalanine from Phenylpyruvic Acid and Ammonia. By EMIL ERLENMEYER, jun., and JULIUS KUNLIN (*Annalen*, 1899, **307**, 146—162).—*α-Phenylacetamidophenylpropionic acid* (*phenylacetylphenylalanine*),

$$CH_2Ph \cdot CO \cdot NH \cdot CH(CH_2Ph) \cdot COOH,$$
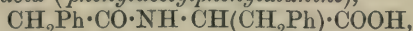
is very sparingly soluble in hot water, crystallises from a mixture of benzene and alcohol in small, colourless needles, and melts at 126°; the *sodium* salt is sparingly soluble in water, and crystallises in aggregates of needles, whilst the *silver* salt is also sparingly soluble, and is sensitive towards light. The *amide* obtained by the action of ammonia either on phenylpyruvic acid or on α-benzamidocinnamic acid, crystallises from hot alcohol in slender, colourless needles, and melts at 186°; the production of this compound from benzamidocinnamic acid is associated with formation of benzamide.

The amide just described is identical with the compound obtained by Plöchl (Abstr., 1886, 351), and first regarded by him as phenylamidolactic acid, but subsequently represented by the formula

$$CHPh{<}{\overset{N-}{\underset{CH}{|}}}{>}CO.$$
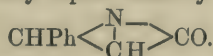
Plöchl obtained the same substance from ammonia and phenylpyruvic acid, which he called phenylglycidic acid, but appears not to have recognised its identity with the compound from benzamidocinnamic acid and ammonia.

When phenylacetylphenylalanine is hydrolysed with concentrated hydrochloric acid at 150°, it is resolved into phenylalanine and phenylacetic acid; contrary to the statement of Plöchl, formic, benzoic, and α-amidocinnamic acids are not formed.　　　　　M. O. F.

Synthesis of Phenylacetylphenylalanine. By EMIL ERLENMEYER, jun., and JULIUS KUNLIN (*Annalen*, 1899, **307**, 163—170. Compare Abstr., 1893, i, 581, and foregoing abstract).—The *lactimide*,

$$CHPh \colon C{<}{\overset{N \cdot CO \cdot CH_2Ph}{\underset{CO}{|}}}$$, prepared by condensing phenaceturic acid
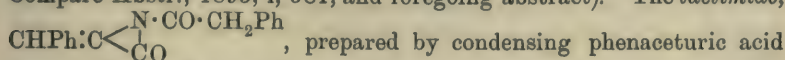
with benzaldehyde under the influence of acetic anhydride and anhydrous sodium acetate, crystallises from alcohol in yellow plates and melts at 105°.

Phenylacetamidocinnamic acid, $CHPh \colon C(COOH) \cdot NH \cdot CO \cdot CH_2Ph$, produced when the lactimide remains in contact with water during several days, separates from alcohol in large, monoclinic crystals melting at 186° [$a : b : c = 1 \cdot 0428 : 1 : 0 \cdot 69247$. $\beta = 68° 3'$]. Reduction

with sodium amalgam converts it into α-phenylacetamidophenylpro-
pionic acid (phenylacetylphenylalanine). M. O. F.

[Tannins]. By HERMANN KUNZ-KRAUSE (*Chem. Centr.*, 1899, i, 559).
—The paper contains a summary of the author's work on the classifi-
cation of tannins.

Ferric chloride is a general reagent for tannins. Certain groups of
tannins which are derived from two or more mols. of protocatechuic
acid by elimination of water are also precipitated by gelatin, albumin
alkaloids, potassium antimony tartrate, and other compounds. The
reactions of these substances and others with gallic, digallic, trigallic,
ellagic, ellagitannic, and chebulic acids, and also with hamamelitannin
and tannin are tabulated. The reactions and decompositions which
tannins undergo in the plants containing them, and particularly the
formation of phlobaphens and "reds," are used, to some extent, as a
basis for classification. The 'reds' are the red to reddish-brown
colouring matters of the bark, which are formed in the same way as
gallotannic acid by a process of dehydration of aromatic hydroxy-
acids. The phlobaphens and reds are both precipitated by gelatin,
and may be obtained from the respective tannins or tannogens by
boiling with dilute sulphuric acid. E. W. W.

Aniline Salts of the Phthalic Acids. By CARL GRAEBE
and J. BUENZOD (*Ber.*, 1899, **32**, 1991—1995. Compare Abstr.,
1897, i, 60).—*Aniline 3-nitrophthalate*, $NO_2 \cdot C_6H_3(COOH)_2, NH_2Ph$,
separates from alcoholic solution in bright yellow flakes and melts
at 180—181° with elimination of water ; the product of decomposition
melts at 132—133°. The salt is insoluble in ether, but readily
soluble in hot water ; the normal salt is not formed even in presence
of a large excess of aniline. No loss in weight occurs on heating at
100°, but at 120—130° it loses water and aniline, and gives a mixture
of a little nitrophthalic acid with *nitrophthalanil* ; this is yellow,
melts at 134°, is insoluble in water, but readily soluble in hot alcohol.

Aniline 4-nitrophthalate melts at 181—182° with loss of water, the
product of decomposition melting at 186—189°. No loss of weight
occurs on heating at 90—100°, but at 120—130° it is converted into
4-nitrophthalanil together with a little nitrophthalic acid ; the
phthalanil crystallises from alcohol and melts at 192°.

Aniline 4-hydroxyphthalate, $OH \cdot C_6H_3(COOH)_2, NH_2Ph$, crystallises
in colourless flakes, dissolves moderately in hot water and readily in
hot alcohol, melts at 159° with loss of water, and remelts at 240°.
4-Hydroxyphthalanil is produced on heating the aniline salt to its
melting point, or by prolonged heating at 100° ; it melts at 251°, is
insoluble in water, but is slightly soluble in cold and readily so in hot
alcohol.

Aniline 4-chlorophthalate melts at 151° and dissolves readily in hot
alcohol. *4-Chlorophthalanil* is produced slowly on heating the aniline
salt at 100° and rapidly at 160—170° ; it melts at 174° and dissolves
fairly readily in hot, but only slightly in cold alcohol.

Normal *aniline 3 : 4-dichlorophthalate*, $C_6H_2Cl_2(COOH)_2, 2NH_2Ph$,
melts and decomposes at 163°, dissolves readily in hot alcohol and hot
water, but only slightly in the cold, and is only very slightly soluble

in ether. On heating at 100°, it loses 1 mol. of aniline, and at 120—130° is converted into 3 : 4-*chlorophthalanil*, which melts at 170—171° and is only slightly soluble in alcohol ; a small amount of the dichlorophthalic acid is also produced.

Normal *aniline tetrachlorophthalate* melts at 263° and is insoluble in water or ether, but moderately soluble in hot alcohol. When heated at 100°, it loses water and a little aniline, and at 120—130° it is converted completely into *tetrachlorophthalanil* melting at 268—269°.

Aniline nitroterephthalate is a colourless salt very readily soluble in alcohol ; when heated, it becomes yellow at 145° and melts at 191° ; when heated at 120°, it loses aniline and is converted completely into nitroterephthalic acid.

Normal *aniline* 2 : 5-*dichloroterephthalate*, forms colourless crystals which decompose at 170—175° and melt at 204—205° ; when heated at 120°, it loses aniline and is converted completely into dichloroterephthalic acid.

Normal *aniline dichlorodihydroterephthalate*,

$$C_6H_4Cl_2(COOH)_2, 2NH_2Ph,$$
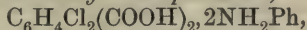
melts at 180° and loses the whole of its aniline when heated at 120°.

Aniline 5-*nitroisophthalate* melts at 165°, remelts at 192—193°, and is very slightly soluble in alcohol.

Isophthalic and terephthalic acids do not combine with aniline.

<div style="text-align:right">T. M. L.</div>

Derivatives of Diphenylmethane. By RICHARD E. MEYER and ALFRED CONZETTI (*Ber.*, 1899, **32**, 2103—2108).—2 : 4 : 2′ : 4′-Tetrahydroxybenzophenone (Abstr., 1897, i, 380) crystallises from water in yellow, glistening needles containing $1\frac{1}{2}H_2O$, and is readily soluble in methylic or ethylic alcohol, ether, acetone, or acetic acid in the cold, and in water, chloroform, benzene, or toluene on warming ; it also dissolves in alkalis and alkali carbonates, yielding non-fluorescent solutions. Although 3 : 6-dihydroxyxanthone is formed when this compound is heated above its melting point, a better yield may be obtained by Graebe's method (Abstr., 1891, 706) ; it dissolves readily in alcohol, acetic acid, or acetone, but is practically insoluble in water, benzene, or toluene ; its solution in concentrated sulphuric acid has a yellow colour and pale blue fluorescence. Its reduction product (compare Kostanecki and Bistrzycki, Abstr., 1885, 1077) appears to be identical with Möhlau and Koch's formaldehydehydroxyfluorone (Abstr., 1895, i, 46). Its *diacetyl* derivative, $C_{13}H_6O_2(OAc)_2$, crystallises from alcohol in colourless, glistening needles melting at 200—202°, and is insoluble in water or alkalis. *Tetrabromo-3 : 6-dihydroxyxanthone*, $C_{13}H_2Br_4O_2(OH)_2$, obtained by gently warming acetic acid solutions of bromine and of dihydroxyxanthone, crystallises in colourless needles melting and decomposing at 280—290° ; it is insoluble in benzene or toluene, but dissolves fairly readily in hot alcohol or acetic acid ; it also dissolves in alkalis, the solutions being colourless, but exhibiting a pale, bluish-violet fluorescence.

Attempts to prepare 3 : 6-dihydroxyxanthone or its derivatives synthetically on the large scale have proved fruitless. The chief product

obtained by condensing β-resorcylic acid with resorcinol in the presence of acetic anhydride is 1 : 6-dihydroxyxanthone. The dibromoresorcinol obtained by the elimination of carbonic anhydride from dibromo-β-resorcylic acid (Zehenter, Abstr., 1882, 193) is identical with that obtained by fusing eosin with alkali (Baeyer, Abstr., 1877, i, 195), the melting point of both being 91·5—92·5°.

Tetrahydroxydinaphthylmethane (methylenedinaphtharesorcinol) has been prepared by Kahl's method; it yields a *tetracetyl* derivative which crystallises in colourless needles, melts at 205—206°, and is only sparingly soluble in most solvents with the exception of acetone.

J. J. S.

Derivatives of Fluoran. By RICHARD E. MEYER and LEO FRIEDLAND (*Ber.*, 1899, 32, 2108—2112. Compare Abstr., 1898, i, 380).—*Nitrofluoran*, $C_{20}H_{11}O_3 \cdot NO_2$, obtained by boiling an acetic acid solution of fluoran with nitric acid of sp. gr. 1·5 for an hour, crystallises in rhombic plates melting at 200—202°, and dissolves in concentrated sulphuric acid, giving a yellow, non-fluorescent solution, but is not soluble in cold alcoholic potash. When reduced with stannous chloride and hydrochloric acid, it yields *amidofluoran*, which crystallises from alcohol in colourless plates melting at 225—228°; it dissolves in cold concentrated sulphuric acid, yielding a yellow solution with a pale green fluorescence, and when warmed turns deep red. When diazotised and boiled with water, it yields fluoran and not hydroxyfluoran.

When fluoran is warmed for some 8 minutes on the water-bath with 10 times its weight of nitric acid of sp. gr. 1·5, and the solution allowed to cool, crystals of 2 : 7-dinitrofluoran separate, and on pouring into water, a flocculent precipitate of *i-dinitrofluoran* is obtained; this crystallises from acetic acid in thick needles melting at 217—220°, and is insoluble in cold alcoholic potash. When reduced with stannous chloride, it yields i-*diamidofluoran*, which crystallises from alcohol in small, rhombic, strongly doubly refractive crystals melting at 237—240°.

2 : 7-*Dinitrohydrofluoranic acid*, $\mathrm{COOH \cdot C_6H_4 \cdot CH} {<}^{C_6H_3(NO_2)}_{C_6H_3(NO_2)} {>} O$, formed when 2 : 7-dinitrofluoran is warmed with alcoholic ammonium sulphide, crystallises from acetic acid in large, yellow, flat needles, melting and decomposing at 245—247°; it is much more readily soluble in alcohol than 2 : 7-dinitrofluoran, and has acid properties. Its solution in cold alcoholic potash is colourless, but turns red when warmed, or on the addition of water.

J. J. S.

Meldola and Hughes' Bromindone Derivatives. By CARL LIEBERMANN and S. SCHLOSSBERG (*Ber.*, 1899, 32, 2095—2102. Compare this vol., i, 372).—The authors have come to the conclusion that the compound described by Meldola and Hughes (Trans., 1890, 396) as bromindone is really β-brom-α-naphthaquinone, and is identical with the compound prepared by Zincke and Schmidt (Abstr., 1895, i, 56) from naphthaquinone dibromide. The bromine atom in bromonaphthaquinone is not readily replaced by aromatic amine residues, and in dibromonaphthaquinone only one of the bromine atoms is readily replaceable by similar residues. Meldola and Hughes' bromindone-

anilide proves to be identical with 2-brom-α-naphthaquinone-3-anilide (compare Miller, Abstr., 1885, 667); it melts at 194°, not at 190°. Their bromohydroxyindone is identical with Merz and Diehl's 2-bromo-3-hydroxynaphthaquinone (Abstr., 1878, 736), the melting point of which is 196—197°, and not 191—192°, and the barium derivative has the composition $(C_{10}H_4BrO_3)_2Ba + 4H_2O$. Their bromindone-β-naphthylamide appears to be 2-brom-α-naphthaquinone-3-naphthyl-amide, which may be obtained from dibrom-α-naphthaquinone; the melting point of the pure compound is about 128°, and not 151° (?).

α-Naphthaquinonebenzylamide, $C_6H_4{<}^{CO \cdot C \cdot NH \cdot CH_2Ph}_{CO \cdot CH}$, obtained from brom-α-naphthaquinone, crystallises in glistening, orange-red needles melting at 156°.

3-Brom-α-naphthaquinone-2-benzylamide, $CH_2Ph \cdot NH \cdot C{<}^{CBr \cdot CO}_{CO-C_6H_4}$, crystallises in orange-red prisms melting at 109°. J. J. S.

Isonaphthazarine, Tetrahydroxynaphthalene, and Tetraketo-hydronaphthalene. By THEODOR ZINCKE and A. OSSENBECK (*Annalen*, 1899, **307**, 1—28. Compare Abstr., 1892, 720).—Isonaphth-azarine (dihydroxynaphthaquinone), $C_6H_4{<}^{CO \cdot C \cdot OH}_{CO \cdot C \cdot OH}$, prepared from β-naphthaquinone, bleaching powder, and hydrochloric acid, crystal-lises from glacial acetic acid in brown leaflets with metallic lustre, and from toluene in slender, red needles; it melts at 280° and sublimes when heated strongly. The solution in caustic alkalis is deep blue, becoming colourless when exposed to air, forming phenylglyoxyl-carboxylic acid; the barium derivative is reddish-violet and sparingly soluble. The *acetyl* derivative crystallises from glacial acetic acid in orange needles and melts at 172°; the *diacetyl* derivative separates from benzene in slender, white needles, and melts at 105°.

Tetrahydroxynaphthalene, $C_6H_4{<}^{C(OH) \cdot C \cdot OH}_{C(OH) \cdot C \cdot OH}$, obtained by reducing isonaphthazarine with zinc and sulphuric acid, crystallises from an ethereal solution on adding light petroleum, forming white, silvery leaflets; it gradually decomposes when heated, yielding isonaphth-azarine, and is very sensitive towards solvents. The *tetracetyl* deriva-tive crystallises in white needles, and melts at 220°. When tetra-hydroxynaphthalene is treated with zinc dust and dilute mineral acids, 1:2:3-trihydroxynaphthalene (naphthapyrogallol) is produced (compare Zincke and Noack, Abstr., 1897, i, 355).

Tetraketohydronaphthalene, $C_6H_4{<}^{CO \cdot CO}_{CO-CO}, 2H_2O$, prepared by oxidis-ing isonaphthazarine with nitric acid of sp. gr. 1·2, crystallises from nitric acid in large, colourless, monoclinic prisms; it is readily soluble in common media, excepting benzene and light petroleum, but the solutions gradually change, yielding isonaphthazarine, which is also formed when the tetraketone is heated at about 135°. The substance dissolves in alkalis and alkali carbonates, forming colourless solutions which rapidly become blue, and, when acidified, yield isonaphthazarine,

which is also obtained by the action of phenylhydrazine on the tetra-ketone; aniline and orthophenylenediamine give rise to $\beta\beta$-anilido-hydroxy-α-naphthaquinone and naphthadiphenazine (Zincke and Wiegand, Abstr., 1895, i, 616). The *dioxime* of tetraketohydro-naphthalene forms lustrous, greyish leaflets, and melts at 228°; the *acetyl* derivative crystallises in colourless needles, and melts at 160°, when it decomposes. *Diketonaphthafurazan*, $C_6H_4\begin{smallmatrix}CO\cdot C:N\\CO\cdot C:N\end{smallmatrix}>O$, pro-duced when the dioxime is heated with acetic anhydride and sodium acetate, crystallises in long, yellowish needles, and melts at 198°.

$\beta\beta$-*Dinitroso-α-naphthaquinone*, $C_6H_4\begin{smallmatrix}CO\cdot C\cdot NO\\CO\cdot C\cdot NO\end{smallmatrix}$, is formed from the dioxime on oxidation with nitric acid, and crystallises from boiling glacial acetic acid in lustrous, yellow leaflets melting at 251°. The *acid* $C_{10}H_6N_2O_5$, obtained by the action of hot, aqueous sodium carbonate on the dinitroso-derivative, melts at 187°, yielding phthalic anhydride; the *silver* salt is crystalline, and the *methylic* salt forms colourless plates melting at 155°. When this acid is reduced with stannous chloride, the *acid* $C_{10}H_8O_5$ is produced; it crystallises in colourless leaflets on adding benzene to the solution in acetone, and melts at 145°. M. O. F.

Constitution of Pinene. By GEORG WAGNER and KAZIMIR SLAWINSKI (*Ber.*, 1899, **32**, 2064—2083. Compare Abstr., 1894, i, 610; 1896, i, 380).—French turpentine oil, boiling at 155—156°, and having a specific rotatory power $[\alpha]_D - 37°\,30'$, has been treated with hypochlorous acid according to a slightly modified method, which is described in detail in the original, and the following compounds have been isolated after treating the mixture with potassium hydroxide: Pinole oxide, sobrerythritol, a chlorhydrin melting at 131—132°, a second chlorhydrin (B), nopinolglycol, and unsaturated compounds.

cis-Pinole oxide is identical with that obtained by Wallach (Abstr., 1896, i, 571), and by Wagner and Ginzberg (this vol., i, 618) from pinol; when hydrated, it yields the same glycol as Wallach (Abstr., 1891, 218; 1892, 998) obtained from pinol bromide, and to the oxide and its product of hydration *cis*-configurations are ascribed, whereas the isomeric glycol obtained by oxidising pinol with dilute perman-ganate is regarded as a *trans*-derivative.

cis-*Sobrerythritol* (*methane*-1 : 2 : 6 : 8-*tetrol*),

$$OH\cdot CMe_2\cdot CH\begin{smallmatrix}CH_2\cdot CH(OH)\\CH_2\cdot CH(OH)\end{smallmatrix}>CMe\cdot OH,$$
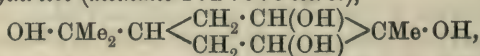
melts at 193—194°, is sparingly soluble in ether, but dissolves readily in alcohol or water; it is optically inactive, yields acetic and ter-penylic acids on oxidation, and is stereoisomeric with the sobrerythritol obtained by the oxidation of inactive sobrerol (Abstr., 1896, i, 446). The chlorhydrin obtained from *l*-pinene melts at 131—132°, and is dextrogyrate, having a specific rotatory power $[\alpha]_D + 88°\,23'$; *d*-pinene yields a chlorhydrin melting at the same temperature, but having the specific rotatory power $-87°\,39'$; the racemate of these two is the chlorhydrin of low melting point previously mentioned (Abstr., 1896, i, 380). The chlorhydrin melting at 131—132°, to which the

constitution CHCl $\begin{cases} \text{CMe(OH)} & \text{CH·O} \\ \text{CH}_2 & | \\ \text{CH}_2 & \text{CH·CMe}_2 \end{cases}$ is given, is not readily

acted on by aqueous alkali. When treated with zinc dust and alcohol for several weeks, it yields pinol as the only product ; this pinol, when oxidised with permanganate, yields an optically active glycol which the authors term d-cistrans-*pinolglycol* ; it melts at 73—74·5°, is readily soluble in ether or ethylic acetate, and is dextrorotatory ; its constitution follows from its products of oxidation, namely, acetic, terpenylic, and terebic acids ; the pinol from which it is derived must be the optically active form of ordinary pinol, although it combines with bromine to give ordinary pinol dibromide melting at 94°.

cis-*Menthane*-1 : 2-*dichlor*-6 : 8-*diol*, crystallises from boiling ether in small, indefinite crystals melting at 136—137° ; when warmed with aqueous potassium hydroxide, it readily loses its chlorine atoms and yields *cis*-pinol oxide ; it is also attacked in the cold by alkalis, but under these circumstances, in addition to pinol oxide, a small amount of a crystalline chlorhydrin is obtained, which is probably identical with the second chlorhydrin (B) formed in minute quantity by the action of hypochlorous acid on pinene. When treated with alcohol and zinc dust, the dichlorhydrin yields *i*-sobrerol and probably limonene.

Nopinolglycol, $\begin{cases} \text{OH·C(CH}_2\text{·OH)} & \text{CH·O} \\ | & \text{CH}_2 & | \\ \text{CH}_2\text{·CH}_2 & \text{CH·CMe}_2 \end{cases}$, is a derivative of

an isomeride of pinene ; it crystallises from ether in prisms melting at 126—127°, is soluble in water, and, when oxidised, yields formic and a non-volatile, syrupy acid, but no acetic acid ; its *acetate* differs from those of the two isomeric pinols in being an oil.

In conclusion, the authors reply to Tiemann's criticisms on their pinene formula. J. J. S.

Crystallography of a Reduction Product of Δ⁴-Terpene-3-one. By WILLIAM H. HOBBS (*Pharm. Arch.*, 1899, **2**, 21—23).—The substance, of which only one crystal admitted of examination, was prepared by Kremers (Abstr., 1897, i, 84), being found in the oily reduction product of Δ⁴-terpene-3-one which had been kept for a year ; it is probably a pinacone. The crystal is a light green, orthorhombic plate [$a : b : c = 0·8857 : 1 : 0·5079$]. T. H. P.

The So-called "Inversion" of Linalool. By EUGÈNE CHARABOT (*Bull. Soc. Chim.*, 1899, [iii], **21**, 549—552. Compare this vol., i, 68). —Attempts were made to obtain an isomeride of linalool by treatment with alcoholic potash. It was found, however, that linalool was unaltered by this reagent. R. H. P.

Nature of the Isomerism of the Two Lemonals (Citrals). By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1899, [iii], **21**, 423—427).—The author discusses his own and Tiemann's investigations on the relation between the two citrals, and concludes that, although it has not been proved that they are not stereoisomerides, it is yet very probable that the isomerism is of a purely chemical nature, and is due to the displacement of a double linking. T. H. P.

Action of Acids on Citral. By ALBERT VERLEY (*Bull. Soc. Chim.*, 1899, [iii], 21, 408—413. Compare Abstr., 1898, i, 557).—*Methyliso-propenecyclohexenol*, $CMe_2:C<^{CH_2———CH_2}_{CH(OH)\cdot CH}>CMe$, formed on mixing citral with ethylic acetate and 50 per cent. sulphuric acid, boils at 96—97° under 12 mm. pressure and has a sp. gr. 0·94612. Its index of refraction for the D line at 16° is 1·397, which gives for the molecular refraction (Lorenz and Lorentz formula) the value 46·99 ; the number calculated from the specific refractions of the constituent atoms is 46·58. It has an agreeable, penetrating odour, recalling orange and bergamot, and quite distinct from that of citral. Its alcoholic nature is shown by its action on sodium, which it dissolves with the liberation of hydrogen and the formation of a sodium derivative. The action of dehydrating agents on it gives rise to cymene. It has the normal molecular weight in benzene.

Citral is reduced by zinc in presence of acetic acid and alcohol, yielding the glycol of citral, 2 : 6 : 11 : 15-*tetramethyl-*2 : 6 : 10 : 14-*octodeca-tetrene-*8 : 9-*diol*, $[CH(OH)\cdot CH:CMe\cdot CH_2\cdot CH_2\cdot CH:CMe_2]_2$, which boils at 203—205° under 15 mm. pressure, has a sp. gr. 0·934 at 0°, and for the D line at 14° its index of refraction is 1·500 ; it dissolves sodium, liberating hydrogen, and has the normal molecular weight in benzene.

T. H. P.

Condensation of Citral with Cyanacetic Acid. By ALBERT VERLEY (*Bull. Soc. Chim.*, 1899, [iii], 21, 413—414).—Cyanacetic acid, citral, and pyridine are heated in a reflux apparatus, the gases evolved being passed first through a wash-bottle containing sulphuric acid to absorb the pyridine, and then through potash tubes to collect the carbonic anhydride. The pyridine is added to stop the polymerising action of the excess of cyanacetic acid. The reaction begins at 95°, and a regular evolution of carbonic anhydride occurs between 100° and 110°, and the heating is stopped when the increase in the weight of the potash tubes corresponds approximately with the theoretical quantity of carbonic anhydride. The liquid is then extracted with ether, and the ethereal solution washed first with dilute sulphuric acid to remove the pyridine, and then with soda solution ; after distilling off the ether and fractionating the residue, the greater part of the liquid passes over at 152—155° under 25 mm. pressure, there being no definite boiling point, owing to polymerisation taking place at each distillation. *Citrylideneacetonitrile*, $C_{12}H_{17}N$, so obtained has a peculiar odour, recalling that of pseudoionone, and when treated with dilute acids, yields no cyclic derivative corresponding to ionone ; concentrated acids cause it to resinify, even in the cold. T. H. P.

Condensation of Citral with Malonic Acid. By ALBERT VERLEY (*Bull. Soc. Chim.*, 1899, [iii], 21, 414—418).—Molecular proportions of citral, pyridine, and malonic acid, when heated together, give rise to citrylideneacetic acid and *citrylidenemalonic acid*, $CMe_2:CH\cdot CH_2\cdot CH_2\cdot CMe:CH\cdot CH:C(COOH)_2$; the latter crystallises from water or alcohol in small, distorted, white prisms melting at 191°. It is insoluble in ether or light petroleum, but is fairly soluble in hot water or alcohol, is very stable towards sulphuric acid or concentrated

potash solution, and loses carbonic anhydride at a temperature above its melting point, yielding citrylideneacetic acid. On treating essence of lemon grass with pyridine and malonic acid, the acid product insoluble in ether contains, in addition to the acid melting at 191°, a smaller amount of an *acid*, $C_{15}H_{24}O_4$, melting at 122°, which is soluble in water or alcohol, fairly so in ether, but insoluble in light petroleum ; it corresponds with an aldehyde homologous with citronellaldehyde, but no such aldehyde could be separated from essence of lemon grass.

Ethylic citrylideneacetate,

$$CMe_2:CH \cdot CH \cdot CH_2 \cdot CH_2 \cdot CMe:CH \cdot CH:CH \cdot COOEt,$$

prepared by heating together ethylic hydrogen malonate, citral, and pyridine in molecular proportion, boils at 160—162° under 24 mm. pressure, and has an odour resembling that of pseudoionone.

Citral readily condenses with acetoacetic acid, giving rise to pseudoionone. T. H. P.

A Polymeride of Citral. By HENRI LABBÉ (*Bull. Soc. Chim.,* 1899, [iii], **21**, 407—408).—On adding, drop by drop, about 100 c.c. of a 1 per cent. alcoholic potash solution to 10 grams of citral, a rise of temperature of 7° or 8° takes place, the original smell of the citral at the same time disappearing and giving way to a slight, although characteristic, odour. When the liquid is diluted with water and extracted with ether, a quantitative yield of a brownish-yellow oil is obtained. This oil does not crystallise, but it is precipitated from a benzene solution by the addition of light petroleum, in the form of an odourless, yellowish-white powder. When thus purified, it softens at 75° and melts between 81° and 82°; its empirical formula is $C_{10}H_{16}O$, the same as that of citral, of which it is a polymeride. From this, it is concluded that condensation of citral with other products cannot be carried out in dilute alcoholic solution of alkali.

T. H. P.

Lemonal from the Essential Oil of Lippia Citriodora. By PHILIPPE BARBIER (*Bull. Soc. Chim.,* 1899, [iii], **21**, 635—638).—The essential oil of *Lippia citriodora*, when fractionally distilled, yields 65 to 70 per cent. of a liquid of the composition $C_{10}H_{16}O$, which boils at 106—108° under 10 mm. pressure, is inactive to polarised light, and has an agreeable odour resembling that of lemons. On oxidation, and on boiling with potassium carbonate solution, this liquid yields the same products as lemonal. With hydroxylamine, it gives two oximes, the one constituting the major portion of the product, boiling at 119—120° under 10 mm. pressure, and the other, which is only obtained in small quantity, being identical with lemonaldoxime boiling at 143—145° under 10 mm. pressure. By the action of sodium hydrogen sulphite, a compound is obtained which, when decomposed with caustic soda, gives an aldehyde convertible into lemonaldoxime boiling at 143—145° under 10 mm. pressure. The oxime from *Lippia citriodora* can also be converted directly into lemonaldoxime by treating its ethereal solution with hydrogen chloride. The oxime boiling at 119—120° dissolves in acetic anhydride without evolution of heat, but only yields a small quantity of the nitrile of citric acid, whilst lemonaldoxime gives, with acetic anhydride, a large evolution

of heat and a good yield of the nitrile. Also the aldehyde from the *Lippia* essence gives a mixture of semicarbazides, consisting mainly of the modification melting at 171°, whilst lemonal yields principally the form melting at 135°.

From these experiments and those of Bouveault (this vol., i, 767), the author concludes that two isomeric lemonals certainly exist, and he is of opinion that they are stereoisomerides.   T. H. P.

Composition of Monarda Oils. By EDWARD KREMERS and W. E. HENDRICKS (*Pharm. Arch.*, 1899, **2**, 73—78).—The oil distilled from *Monarda punctata*, L., contains about 60 per cent. of phenols, consisting mainly of thymol, a little carvacrol sometimes being present. About 10 per cent. of the remainder is an alcoholic compound, the rest, which boils at 170—180°, consisting of cymene and a small quantity of dextrorotatory limonene.

Monarda fistulosa, L., yields an oil containing cymene, carvacrol, and limonene; if thymol is present, its amount must be less than 2 per cent. of that of the carvacrol.   T. H. P.

Combination of Camphor with Aldehydes. By ALBIN HALLER (*Compt. rend.*, 1899, **128**, 1270—1274).—The author has previously shown (Abstr., 1891, 1498) that crystalline compounds are formed by the interaction of sodiocamphor with various aldehydes of the benzene series. Since the sodiocamphor is mixed with sodioborneol, campholic salts of the acids corresponding with the aldehydes employed are amongst the products. In the case of piperonaldehyde, for example, piperonylic alcohol and piperonylic piperonylate are formed.

The action of meta- or para-methoxybenzaldehyde on sodiocamphor yields a *methoxybenzylidenecamphor*, $C_8H_{14} <\begin{smallmatrix} C:CH \cdot C_6H_4 \cdot OMe \\ CO \end{smallmatrix}$. The meta-derivative forms long, white needles which melt at 51—52° and are much more soluble in organic solvents than the ortho- or para-compounds, the para-derivative forms rhombic crystals with an angle 114·45°, and melts at 125°. When treated with sodium amalgam in presence of alcohol, each is reduced to a *methoxybenzylcamphor*, $C_8H_{14} <\begin{smallmatrix} CH \cdot CH_2 \cdot C_6H_4 \cdot OMe \\ CO \end{smallmatrix}$; the meta-derivative is an oily liquid which boils at 205—206° under 10 mm. pressure, and the para-derivative forms rhombic prisms with an angle of 105·45° which melt at 71°. It is noteworthy that in the two sets of compounds the meta-derivative has the lowest and the para-derivative the highest melting point.

Piperonylidenecamphor, $C_8H_{14} <\begin{smallmatrix} C:CH \cdot C_6H_3:O_2:CH_2 \\ CO \end{smallmatrix}$, obtained in a similar manner, forms colourless needles which melt at 159·5°. When reduced, it yields the corresponding piperonylcamphor which crystallises in small, white lamellæ melting at 70°.

Piperonylic piperonylate crystallises in needles, melts at 97° and is hydrolysed by alcoholic potash; cryoscopic measurements show that its molecular weight is 300. Piperonylic alcohol crystallises in white, flattened needles which melt at 51—52°.

All the aldehydic derivatives of camphor are characterised by the ease with which they are reduced to alkylic camphors, the reduction affecting first the group C:C and afterwards the CO group.

<div align="right">C. H. B.</div>

Corrosion Figures showing the Enantiomorphous Structure of Benzylidenecamphors. By JULES MINGUIN (*Compt. rend.*, 1899, **128**, 1335—1336).—When optically active benzylidenecamphor is immersed for about a minute in benzene, the crystals show, on the faces *m*, corrosion figures which are distinctly unsymmetrical, the figures being generally directed from the angle *a* to the angle *e* of the prism. The figures formed on the dextrogyrate compound are enantiomorphous with those formed on the lævogyrate compound. No precise results have as yet been obtained with faces other than *m*.

<div align="right">C. H. B.</div>

Desmotropic Forms of Camphor Methylenephenylhydrazone. By MARIO BETTI (*Ber.*, 1899, **32**, 1995—1999).—The product of the action of diazobenzene chloride on sodium camphorcarboxylate melts at 165°, but when recrystallised from alcohol, it separates in stout, brownish-yellow needles and melts at 180°; the melting point is unchanged by crystallising from benzene. When dissolved in cold benzene, the substance gives a deep ruby-red coloration with ethereal ferric chloride and is therefore regarded as the *enolic form* of camphor *methylene-* or *a-phenylhydrazone*, $C_8H_{14} < \begin{matrix} C \cdot N \colon N \cdot Ph \\ \| \\ C \cdot OH \end{matrix}$.

When a trace of piperidine is added to a solution of the substance in benzene, small, yellow crystals are deposited which melt at 155° and give no immediate coloration with ferric chloride, although the characteristic red coloration of the enolic form appears after some hours. The form melting at 155° is regarded as the *ketonic* modification, $C_8H_{14} < \begin{matrix} C \colon N \cdot NHPh \\ \| \\ CO \end{matrix}$.

The ketonic, like the enolic, form can be crystallised unchanged from benzene, but on crystallising twice from 95 per cent. alcohol the enolic form melting at 180° is deposited.

A *mixture* of the two forms, melting at 167°, is produced on crystallising the enolic form from glacial acetic acid; a similar mixture is produced on precipitating a cold alcoholic solution of the enolic form with dilute potash, but water alone precipitates the enolic form. A mixture melting at 165° is produced by heating either the enolic or the ketonic form at the melting point for some time, and then crystallising from benzene, and also by crystallising the ketonic form repeatedly from benzene.

<div align="right">T. M. L.</div>

Action of Certain Gases on Caoutchouc. By A. D'ARSONVAL (*Compt. rend.*, 1899, **128**, 1545—1546).—When caoutchouc is left for a time in carbonic anhydride at pressures of from 1 to 50 atmospheres, it absorbs large quantities of the gas and swells considerably, in some cases having expanded to as much as 10 or 12 times the original volume. After this treatment, the caoutchouc is more gelatinous and less elastic than before, and, on leaving it in the air,

bubbles of carbonic anhydride are given off with a faint noise. Carbonic anhydride at ordinary pressure readily passes through a caoutchouc bag, the rate of deflation increasing with the pressure of the gas. With oxygen, the escape is less rapid, and still less so with nitrogen, this last being hence recommended for the inflation of pneumatic tyres. T. H. P.

Cerin and Friedelin. By CONSTANTIN I. ISTRATI and ADRIANO OSTROGOVICH (*Compt. rend.*, 1899, **128**, 1581—1584).—By extracting cork with chloroform and fractionally crystallising the extract, cerin and friedelin were obtained.

Cerin is a white, silky substance melting at 234—234·5° (corr.), and is slightly soluble in ethylic alcohol, acetate, or ether, but more so in chloroform, benzene, ethylenic bromide, nitrobenzene, or phenol. It has the composition $C_{27}H_{44}O_2$, which agrees with the molecular weight determined by the boiling point method (the compositions previously assigned to it were: Döpping, $C_{25}H_{20}O_3$; Siewert, $C_{17}H_{28}O$; Kügler, $C_{20}H_{32}O$; and Thoms, $C_{30}H_{50}O_2$, or $C_{32}H_{54}O_2$). The specific rotatory power in chloroform solution varies with the concentration, having at 24° its maximum value − 84·69° for a saturated 0·3306 per cent. solution; a supersaturated 0·431 per cent. solution gives a specific rotation −81·20°.

Friedelin, $C_{48}H_{70}O_2$, which is the fraction more soluble in chloroform, crystallises from alcohol in long, flat, brilliant needles melting at 263—263·5° (corr.). It is soluble in the same solvents as cerin, but to a greater extent, and in chloroform solution has the normal molecular weight. The specific rotation in chloroform at 24° has its maximum value − 48·72° for a 0·821 per cent. solution.

Of the two reactions given by Thoms (this vol., ii, 324) for his cerin, one is given by both cerin and friedelin, namely, the formation of a rose-red coloration on the addition of concentrated sulphuric acid to an acetic anhydride solution of the substance; but neither of the authors' compounds gives with a mixture of chloroform and sulphuric acid a yellow colour changing to violet. T. H. P.

Study of Ivy: Preparation of Hederin. By HOUDAS (*Compt. rend.*, 1899, **128**, 1463—1465).—The author has separated from ivy a glucoside, *hederin*, $C_{64}H_{104}O_{19}$, which crystallises from alcohol in long, radiating groups of thin needles, and melts at 248° to a slightly amber-coloured liquid; a determination of the molecular weight by the ebullioscopic method agreed with the formula given. Hederin has an almost imperceptible, sweetish flavour, and in alcoholic solution at 22° has $[\alpha]_D + 16·27°$. It is insoluble in water, light petroleum, or chloroform, but dissolves slightly in ether or benzene, and more so in alcohol or acetone. It is readily dissolved by hot alkaline hydroxides or carbonates. When boiled for 12 hours with 4 per cent. sulphuric acid in a reflux apparatus, hederin gives rise to an insoluble product, hederidin, and to two sugars, hederose and rhamnose.

Hederidin, $C_{26}H_{40}O_4$, crystallises from boiling alcohol in sparkling rhomboidal prisms which are insoluble in water, ether, benzene, or chloroform; these melt at 324° and sublime undecomposed.

Hederose, $C_6H_{12}O_6$, crystallises in shining, concentrically grouped needles, and is very soluble in water or boiling alcohol. It melts at 155°, and in solution exhibits birotation; the boiled solution at 22° gives $[a]_D + 102\cdot66$. ⟶ ⟶ ⟶ ⟶ ⟶ ⟶ ⟶ **T. H. P.**

Formation of Pyrroline and Pyrrolidine Derivatives from Triacetonamine. I. By HERMANN PAULY and JOSEPH ROSSBACH (*Ber.*, 1899, **32**, 2000—2014. Compare Abstr., 1898, i, 382).—The substance previously described (*loc. cit.*) as 'iminotriacetonamine' is shown to be *a-tetramethylpyrroline-β-carboxylamide*,

$$NH\!\!<\!\!\begin{array}{l}CMe_2\cdot CH\\CMe_2\cdot C\cdot CO\cdot NH_2\end{array}\cdot$$
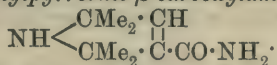
It decolorises potassium permanganate in acid solution, does not interact with hydroxylamine, phenylhydrazine, or hydrogen cyanide, and has a normal molecular weight in boiling benzene. The *monacetyl* derivative is precipitated by ether from acetic acid solution in crystalline aggregates and melts at 256—256·5°. The *mononitrosamine* crystallises from acetone in fine, white needles and melts at 201°. The *perbromide*, $C_9H_{16}ON_2,HBr,Br_2$, crystallises from glacial acetic acid in yellowish-red flakes and melts at 201°; it is very stable in the dry state, but loses bromine when boiled with water or acetone; by prolonged heating at 120°, it loses 1 mol. of bromine and leaves the hydrobromide of the base; the bromine test gives, therefore, no indication of the double bond.

The *hydriodide* of *1-methyl-a-tetramethylpyrroline-β-carboxylamide*,

$$NMe\!\!<\!\!\begin{array}{l}CMe_2\cdot CH\\CMe_2\cdot C\cdot CO\cdot NH_2\end{array}\!,HI,$$ crystallises from a mixture of methylic

alcohol and ethylic acetate in fine needles, and dissolves very readily in water and alcohol; it becomes yellowish when dried at 110° and melts at 221—222°. The methylated *base* crystallises from light petroleum in rhombic tablets, dissolves very readily in water, alcohol, ether, acetone, or boiling benzene, and melts at 104°; when a solution in light petroleum is dried over potash, the *potassium salt* of the base separates as a white powder (compare pyrrole and benzamide), but is decomposed by water. All the salts are very soluble.

Tetramethylpyrrolinecarboxylmethylamide, $NH\!\!<\!\!\begin{array}{l}CMe_2\cdot CH\\CMe_2\cdot C\cdot CO\cdot NHMe\end{array}'$

isomeric with the preceding base, is produced by the action of methylamine on dibromotriacetonamine; it separates from ether in silky, thread-like needles which melt at 66—67°, and distils undecomposed in a vacuum, the melting point rising to 78°. The *aurichloride* crystallises in prisms, and when dried over sulphuric acid melts at 190°.

a-Tetramethylpyrrolidine-β-carboxylamide, $NH\!\!<\!\!\begin{array}{l}CMe_2\cdot CH_2\\CMe_2\cdot CH\cdot CO\cdot NH_2\end{array}'$

produced by reduction of the pyrroline base with sodium amalgam, crystallises from toluene and melts at 121°, but when dried by distillation in a vacuum, melts at 129—130°; it is slightly soluble in water, benzene, toluene, or ether, but readily in alcohol or acetone. The *hydrochloride* is easily soluble in water, less readily in alcohol. The

hydrobromide forms small, glistening, prismatic crystals and melts at 256°. The *picrate* separates from water in yellow, glistening prisms and melts at 189°. The *aurichloride*, $C_9H_{18}ON_2,HAuCl_4$, crystallises from water in large, golden-yellow, flat needles and melts at 210°. The *platinochloride*, $(C_9H_{18}ON_2)_2,H_2PtCl_6$, crystallises from alcohol in orange-yellow, rhombic tablets, and dissolves readily in water, but deposits ammonium platinochloride on boiling the solution. *Nitroso-tetramethylpyrrolidinecarboxylamide* crystallises from water in slender, white needles and melts at 229°.

The *hydriodide* of 1-*methyl-a-tetramethylpyrrolidine-β-carboxylamide* $NMe\!<^{CMe_2 \cdot CH_2}_{CMe_2 \cdot CH \cdot CO \cdot NH_2}, HI$, crystallises from 80 per cent. alcohol in short, glistening prisms and melts at 250°; it dissolves easily in water and less readily in alcohol and wood spirit. The *base* crystallises from acetone in slender needles and melts at 142—144°, but can only be dried completely by distillation in a vacuum; it does not decolorise acid potassium permanganate solution, and is not acted on by nitrous acid. The *picrate* crystallises from alcohol in hair-like needles and melts at 160°. The *aurichloride* crystallises in quadratic tablets and melts at 172°. The *platinochloride* separates in brown, microscopic prisms and melts at 227°.

Tetramethylpyrrolinecarboxylamide is most readily hydrolysed by aqueous alkalis, but can also be hydrolysed by heating at 130° with concentrated hydrochloric acid. The *hydrochloride* of *a-tetramethyl-pyrroline-β-carboxylic acid*, $NH\!<^{CMe_2 \cdot CH}_{CMe_2 \cdot C \cdot COOH}, HCl + 2H_2O$, crystallises from water in well-formed, thick, six-sided tablets. The *aurichloride*, $C_9H_{15}NO_2,HAuCl_4,H_2O$, crystallises in slender, golden needles, sinters at 150°, and melts at 185°. The *acid* crystallises from hot water as a glistening powder and melts at 300°; it is much more readily soluble in cold water, and on evaporation the solution deposits fine, well-formed, thick, monoclinic prisms, or large six-sided tablets containing $2H_2O$. The *methylic* salt boils at 201° under 740 mm. pressure, and forms an insoluble, mobile, colourless fluid, with a faint, stupefying odour; the *ethylic* salt boils at 212° under 740 mm. pressure, and when acted on with ammonia in methylic alcohol, re-forms the original amide. T. M. L.

Derivatives of Picoline. By ARNOLD HESS (*Ber.*, 1899, **32**, 1985—1987).—*Nitroso*-4 : 6-*dihydroxy-2-picoline*, prepared by the action of nitrous acid on dihydroxypicoline, is a yellow powder readily soluble in water; it dissolves in alkalis to a green solution, is only slightly soluble in hydrochloric and sulphuric acids, and is insoluble in light petroleum; with ferric chloride, it gives a green solution and a dark precipitate; it crystallises from alcohol in glistening, brown scales, but on boiling the solution decomposition occurs, and a dark-coloured substance separates which contains a smaller percentage of nitrogen; on heating, the nitroso-compound explodes without melting. By the action of stannous chloride and hydrochloric acid, the nitroso-compound is not reduced, but is converted into a *trihydroxypicoline*, which crystallises from water in violet needles and melts at 263—265°;

with ferric chloride, it gives an intense blue coloration, which becomes red in alkaline and green in acid solution; the blue colour disappears on heating the solution, but reappears on cooling, the first appearance of colour being on the surface exposed to the oxidising action of the air. The *hydrochloride* forms large, rhombic crystals, which melt at 85—90°, lose water and hydrogen chloride at 100°, and finally melt at 263—265°.

The trihydroxypicoline is isomeric with that described by Sedgwick and Collie (Trans., 1895, **67**, 412) which melts at 179°, but is perhaps identical with their compound melting at 252° (corr. 262°).

<div align="right">T. M. L.</div>

Quinazoline Compounds. By GOTTFRIED HANSCHKE (*Ber.*, 1899, **32**, 2021—2030. Compare Fröhlich, Abstr., 1885, 154).—6-*Amido-3-methylbenzophenone*, $NH_2 \cdot C_6H_3Me \cdot CO \cdot CH_3$, is readily soluble in ether, alcohol, chloroform, acetone, acetic acid, or light petroleum, crystallises in yellow needles or long, six-sided tablets, sinters at 60°, and melts at 64°. The *hydrochloride* forms white needles which melt and decompose at 179—180°, becomes yellowish-brown in the air, and is decomposed by water. The *picrate* forms yellow prisms and melts at 145°. The *benzoyl* derivative separates from alcohol in cubes or slender needles, and melts at 114—116°.

4′-*Phenyl-3-methyl-2′-ketodihydroquinazoline*, $C_6H_3Me{<}^{CPh:N}_{NH-CO}$, produced by heating the base with carbamide, crystallises from alcohol in colourless prisms and melts at 283—285°; it is insoluble in water or ether, slightly soluble in alcohol, readily in acetic acid, and is dissolved by alkalis and acids, the latter giving a yellow solution. The *hydrochloride* forms yellow needles, and is dissociated by heating, and slowly when left in a vacuum over lime. The *nitrate* separates in yellow, glistening needles, and froths up when heated to 200°, leaving a substance which melts at 250°. The *dichromate* crystallises in orange-coloured needles or flakes. The *benzoyl* derivative crystallises from alcohol in flat needles or rhombic tablets, and melts at 121—122°.

2′-*Chloro-4′-phenyl-3-methylquinazoline*, $C_6H_3Me{<}^{CPh:N}_{N=CCl}$, crystallises from alcohol in slender, colourless needles and melts at 140—141°; it dissolves in acids, but is reprecipitated by water.

4′-*Phenyl-3-methyl-3′ : 4′-dihydroquinazoline*, $C_6H_3Me{<}^{CHPh \cdot NH}_{N==CH}$, separates from alcohol in stout, well-formed crystals, and melts at 186—188°; the base, like its salts, is only slightly soluble in water, and has a bitter taste. The *hydrochloride* melts at 240°. The *nitrate* is even less soluble than the hydrochloride; it melts at 186° with vigorous frothing. The *picrate* crystallises from alcohol and melts at 173—175°, but sinters at a lower temperature. The *dichromate* separates as a yellow powder, which becomes brown on the surface when exposed to air. The *ferrocyanide* forms colourless, well-formed crystals. The *benzoyl* derivative crystallises from alcohol in thread-like needles and melts at 185—186°.

6-*Amido-3-methylbenzhydrol*, $NH_2 \cdot C_6H_3Me \cdot CHPh \cdot OH$, separates

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from dilute alcohol in white, ill-defined crystals, and melts at 82—84°; it dissolves in hydrochloric acid, but does not form a stable salt, and decomposes on boiling the solution, emitting an odour of benzaldehyde.

$4'$-*Phenyl-3-methyl-2'-ketotetrahydroquinazoline*, $C_6H_3Me\diagdown\begin{smallmatrix} CHPh\cdot NH \\ NH——CO \end{smallmatrix}$,

produced by heating the benzhydrol with carbamide, crystallises from alcohol in square leaflets and melts at 206—207°. The *acetate*, $C_{15}H_{14}N_2O,C_2H_4O_2$, softens at 120° and melts at 190°. The *picrate* crystallises from alcohol in yellow needles and melts at 157—158°.

$4'$-*Phenyl-3-methyl-2'-thiotetrahydroquinazoline*, $C_6H_3Me\diagdown\begin{smallmatrix} CHPh\cdot NH \\ NH——CS \end{smallmatrix}$,

prepared by the action of thiocyanic acid on the benzhydrol, separates from hot acetic acid in stout, well-developed crystals, dissolves slightly in alcohol, but not in water, becomes brown at 240°, sinters at 250°, and melts at 265—270° with evolution of gas. By the action of bromine, it is converted into the $4'$-*phenyl-3-methyl-2'-bromodihydro-quinazoline hydrobromide*, $C_6H_3Me\diagdown\begin{smallmatrix} CHPh\cdot NH \\ N══CBr \end{smallmatrix},HBr$, which separates

from the acetic acid solution in large, well-formed rhombohedra, dissolves readily in alcohol, becomes brown on heating, sinters at 240°, and melts at 255°. The *base* crystallises from alcohol in slender prisms and melts at 155°. By the action of sodium carbonate on the alcoholic solution, the bromine is removed, and $4'$-phenyl-3-methyl-2'-ketotetrahydroquinazoline is produced. Reduction with hydriodic acid and phosphorus gives $4'$-phenyl-3-methyldihydroquinazoline.

By the condensation of phthalylparatoluidide with benzoic chloride, there is produced, in addition to the phthalyl derivative of 6-amido-3-methylbenzophenone, an isomeric base, which is probably 5-*amido*-2-*methylbenzophenone* (?). The base, which was obtained as a yellow oil, gives a *benzoyl* derivative which separates from alcohol in white needles and melts at 136—138°. The *sulphate* melts at 147—149°, dissolves unchanged in cold water, but is partly decomposed on boiling the solution. The *hydrochloride* melts between 120° and 150°.

<div align="right">T. M. L.</div>

1-Ethylphthalazine and some Derivatives of Phthalazone. By VICTOR PAUL (*Ber.*, 1899, **32**, 2014—2021. Compare Abstr., 1898, i, 211).—$4'$-*Chlorophthalazine picrate*, $C_6H_4\diagdown\begin{smallmatrix} CH:N \\ CCl:N \end{smallmatrix},C_6H_3N_3O_7$,

crystallises in long needles and melts at 135°. The *platinochloride*, $(C_8H_5ClN_2)_2,H_2PtCl_6$, separates in orange-yellow needles and melts at 205°. The *ferrocyanide*, $(C_8H_5N_2Cl)_2,H_4Fe(CN)_6$, forms orange-yellow needles which, when heated, decompose without melting.

Phthalazine *hydriodide*, $C_6H_4\diagdown\begin{smallmatrix} CH:N \\ CH:N \end{smallmatrix},HI$, forms lemon-yellow

crystals, dissolves readily in water, becomes brown at 200°, and melts at 203°. The *ferrocyanide*, $(C_8H_6N_2)_2,H_4Fe(CN)_6$, forms yellow prisms and has no melting point. The *aurichloride*, $C_8H_6N_2,HAuCl_4$, forms yellow needles and melts at 200°.

$4'$-*Chlorethylphthalazine* is obtained from $1'$-ethylphthalazone

(m. p. 168—169°) by heating with phosphorus oxychloride (Abstr., 1898, i, 212); it melts at 93°. The *hydrochloride*, $C_{10}H_9N_2Cl,HCl$, dissolves very easily in water, crystallises from absolute alcohol in stout needles, and melts at 183—184°. The *aurichloride*, $C_{10}H_9N_2Cl,HAuCl_4$, separates in yellow needles, melts at 116°, and decomposes with frothing at 150°. The *platinochloride*, $(C_{10}H_9N_2Cl)_2,H_2PtCl_6$, is golden-yellow. The *ferrocyanide*, $(C_{10}H_9N_2Cl)_2,H_4Fe(CN)_6$, crystallises in orange-coloured needles. The *picrate*, $C_{10}H_9N_2Cl,C_6H_3N_3O_7$, separates in yellow needles. The *dichromate*, $(C_{10}H_9N_2Cl)_2,H_2Cr_2O_7$, forms orange-coloured needles which explode without melting.

4′ : 1′-*Iodoethylphthalazine*, $C_6H_4{<}^{CEt:N}_{CI=N}$, melts at 78°. The *hydriodide*, $C_{10}H_9N_2I,HI$, forms feebly-soluble, orange-yellow needles which darken at 175° and melt at 178°. The *hydrochloride* forms yellow needles and melts at 173°; it is somewhat more soluble than the hydriodide. The *picrate* separates in long, yellow needles, and melts at 141°. The *platinochloride* forms yellow needles.

1′-*Ethylphthalazine*, $C_6H_4{<}^{CEt:N}_{CH=N}$, distils at 206° under 25 mm. pressure, and at 190° under 16 mm. pressure, but decomposes when distilled under atmospheric pressure; it solidifies in a vacuum to a hard mass melting at 23·5°; the base is miscible with water, does not reduce Fehling's solution, becomes brown in the air, dissolves readily in ordinary solvents, has a neutral reaction, and an odour resembling that of acacia blossoms. The *hydriodide* is precipitated by ether from its alcoholic solution in yellow needles which become brown at 200° and melt at 203°. The *hydrochloride* dissolves readily in water, crystallises from 96 per cent. alcohol in colourless prisms, and melts at 216°. The *picrate* forms golden-yellow needles and melts at 175° with evolution of gas. The *platinochloride* separates in slightly soluble, orange-coloured needles, and melts with frothing at 180°. The *aurichloride* forms golden-yellow needles, melts at 144°, and decomposes at 175°. The *dichromate* forms slightly soluble, orange-coloured needles which explode when heated rapidly. The *ferrocyanide* forms sparingly soluble, yellow needles.

1′-*Ethyltetrahydrophthalazine*, $C_6H_4{<}^{CHEt\cdot NH}_{CH_2-NH}$, is an oil which does not appear to form any insoluble salts. The *hydrochloride* forms colourless crystals, melts at 168°, dissolves very readily in water, and reduces Fehling's solution in the cold. The *dibenzoyl* derivative separates from alcohol in pointed columns and melts at 159°. The *methiodide*, $C_{10}H_{10}N_2,MeI$, separates from benzene solution in long, golden-yellow needles, becomes red at 117°, melts at 129°, and dissolves readily in water. The corresponding *picrate* forms golden-yellow needles and melts at 171°.

By the action of caustic potash, ethylphthalazine methiodide is converted into 3′-*methyl*-1′-*ethyldihydrophthalazine*, $C_6H_4{<}^{CEt:N}_{CH_2\cdot NMe}$, and 3′-*methyl*-1′-*ethylphthalazone*, $C_6H_4{<}^{CEt:N}_{CO-NMe}$.

The *picrate* of 3-methyl-1-ethyldihydrophthalazine crystallises from alcohol in alizarin-red needles and melts at 108°; the *platinochloride* forms long, golden-yellow needles; the *ferrocyanide* forms yellow needles which decompose without melting. 3'-Methyl-1'-ethylphthalazone, unlike the dihydro-base, is not volatile with steam; it forms crystals melting at 78—79°, and distils without decomposition.

The ethylation of phthalazone gives 3'-ethylphthalazone and the ethiodide described below. *3'-Ethylphthalazone*, $C_6H_4 {<} {CH:N \atop CO \cdot NEt}$, distils at 295° and solidifies to a colourless, crystalline mass which melts at 55°. *Hydrazophthalaldehydic acid ethiodide*,

$$COOH \cdot C_6H_4 \cdot CH:N_2H_2,EtI,$$
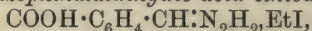
is precipitated in needles on adding ether to a cold, alcoholic solution, becomes yellow, and melts at 171°, losing water and ethylic iodide, after which it melts again at 181°, the melting point of phthalazone.

<div align="right">T. M. L.</div>

Camphopyrazolones. By H. WAHL (*Ber.*, 1899, **32**, 1987—1991). —1-*Phenyl*-4 : 5-*campho*-3-*pyrazolone*, $C_8H_{14} {<} {C-CO \atop C \cdot NPh} {>} NH$, produced by heating together ethylic camphorcarboxylate and phenylhydrazine, crystallises from acetic acid and melts with partial decomposition at 285°.

1-*Phenyl*-4 : 5-*campho*-3-*benzoyloxypyrazole*, $C_8H_{14} {<} {C \cdot C(OBz) \atop C - NPh} {>} N$, prepared by the action of benzoic chloride and potash on the pyrazolone, crystallises from dilute alcohol in needles and melts at 111·5°. The *methiodide* melts and decomposes at 175°, and when warmed with dilute sodium hydroxide is converted quantitatively into 1-*phenyl-2-methyl-*4 : 5-*campho-3-pyrazolone* (camphoisoantipyrine), $C_8H_{14} {<} {C-CO \atop C \cdot NPh} {>} NMe$; this crystallises from dilute alcohol or from ethylic acetate in well-formed tablets, melts at 182—183°, dissolves slightly in hot water, and gives a dark-red coloration with ferric chloride.

1-*Phenyl*-3 : 4-*campho*-5-*pyrazolone*, $C_8H_{14} {<} {C \cdot NH \atop C-CO} {>} NPh$, prepared by the action of phosphorus trichloride on ethylic camphocarboxylate and phenylhydrazine dissolved in toluene, crystallises from alcohol in minute needles and melts at 152°. 1-*Phenyl*-3 : 4-*campho*-5-*benzoyloxy-pyrazole*, $C_8H_{14} {<} {C - NH \atop C \cdot C(OBz)} {>} NPh$, crystallises from dilute alcohol in white flakes and melts at 121—122°. The *methiodide* melts and decomposes at 170°. 1-*Phenyl-2-methyl-*3 : 4-*campho-5-pyrazolone* (campho-antipyrin), $C_8H_{14} {<} {C \cdot NMe \atop C - CO} {>} NPh$, crystallises from alcohol in white, glistening needles, melts at 193°, dissolves slightly in hot water, and gives a brownish-red coloration with ferric chloride.

The methylated campho-3-pyrazolone, like the so-called isoantipyrine, is poisonous, but the 5-pyrazolone has a physiological action like that of antipyrine.

<div align="right">T. M. L.</div>

Synthetical Bases of the Series of Terpenes and Camphors. By PAUL DUDEN and W. PRITZKOW (*Annalen*, 1899, **307**, 207—230. Compare this vol., i, 626).—*Dihydrodicamphenepyrazine*,

$$C_8H_{14} < \begin{matrix} CH \cdot N : C \\ | \quad \quad | \\ C : N - CH \end{matrix} > C_8H_{14},$$
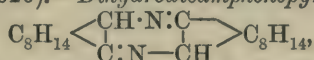
prepared by heating amidocamphor on the water-bath during 5 hours, is also produced when the primary base is exposed to summer temperatures during several days, and crystallises from ether or petroleum in colourless prisms melting at 116°; it is not very volatile in steam, and is indifferent towards mercuric oxide, ammoniacal silver solution, and Fehling's solution. Methylic iodide unites with dihydrodicamphenepyrazine, forming a yellow oil, which is resolved at 200° into methylic iodide and dicamphenepyrazine. The *monohydrochloride* crystallises from water in long, flat prisms, melts at 258°, and is acid towards towards litmus; the *dihydrochloride* melts at 260°, and loses 1HCl in a desiccator. The *nitrate* forms colourless needles, decomposing at 88°, and the *picrate* crystallises from alcohol in lustrous leaflets; the *silver nitrate* compound, $C_{20}H_{30}N_2,AgNO_3$, crystallises in long, slender needles, containing $1H_2O$, and decomposes at 187°.

Dicamphenepyrazine, $C_8H_{14} < \begin{matrix} C \cdot NH \cdot C \\ || \quad \quad || \\ C \cdot NH \cdot C \end{matrix} > C_8H_{14}$, obtained by oxidising dihydrodicamphenepyrazine with ferric chloride, crystallises from alcohol in long needles and melts at 157°, boiling at 326° under 748 mm. pressure; reduction with tin and hydrochloric acid regenerates the dihydro-derivative. The *hydrochloride* is a crystalline powder, the *platinochloride* forms orange prisms, and the *aurichloride* decomposes at 240°; the *mercurichloride* crystallises from dilute alcohol in colourless needles and decomposes at 249°. The *silver nitrate* compound crystallises in thin, four-sided plates, and melts above 270°. The *methiodide* crystallises from water in concentric aggregates of long needles containing $1H_2O$; the *platinochloride* of the ammonium base crystallises from dilute hydrochloric acid in small prisms and decomposes above 260°.

Dicamphanepyrazine, $C_8H_{14} < \begin{matrix} CH \cdot NH \cdot CH \\ | \quad \quad \quad | \\ CH \cdot NH \cdot CH \end{matrix} > C_8H_{14}$, prepared by reducing the foregoing pyrazine bases in alcoholic solution with sodium, melts at 147°; the *hydrochloride* crystallises from alcohol in slender needles, remaining unfused at 275°, and the *nitrate* crystallises in long needles, and melts, evolving gas, at 180°. The *sulphate* forms prisms; the *picrate* crystallises from water in thin, lustrous leaflets, and decomposes at 235°; the *dinitrosamine* separates from alcohol in thin, six-sided plates melting at 215°. M. O. F.

Coloured Salts of Violuric Acid and other Oximidoketones. By J. GUINCHARD (*Ber.*, 1899, **32**, 1723—1741).—*Oximidomethyl-isoxazolone*, $NOH : C < \begin{matrix} CO \cdot O \\ CMe \end{matrix} > N$, is a colourless substance, but gives a red solution with alkalis which is decolorised when the alkali is in excess owing to the formation of a colourless salt of methylglyoxime-carboxylic acid, $NOH : CMe \cdot C(NOH) \cdot COOH$. The *potassium* salt, to

which the formula $\text{N:C·CMe:N}^{\text{O·C(OK)·O}}$ is assigned, separates from alcohol as
a rosy-red powder which slowly decomposes with evolution of hydrogen
cyanide; with water it gives a red solution which slowly loses its
colour, the solutions in ethylic and methylic alcohols are more stable.
The *acid potassium* salt, $C_4H_3N_2O_3K + C_4H_4N_2O_3$, is yellow, but is split
up into its components by water and gives a red solution. It also yields
a yellow *acid* and a red *normal* ammonium salt. The *silver* salt, when
treated with methylic iodide, gives a colourless *methylic* salt,
$\text{NOMe:C}\diagdown^{\text{CO·O}}_{\text{CMe}}\diagup\text{N}$, which crystallises from light petroleum and melts
at 65—66°; it is only slightly soluble in water or light petroleum,
but readily in alcohol and ether; it slowly dissolves in alkalis, giving
a colourless solution of a salt of the acid $\text{NOH:CMe·C(:NOMe)·COOH}$,
but on acidifying and extracting with ether, the original methylic salt
is recovered.

The change of methyloximidoxazolone into methylglyoximecarboxylic
acid has been studied by means of conductivity determinations; the change
is unimolecular and proceeds rapidly at first, even at 0°, but is not
complete even after several months, since the solution always develops
the red colour of the erythro-salt on adding ammonia; the equilibrium
which therefore exists between the two acids can also be reached in the
other direction, for a colourless alkaline solution of the open-chain
acid, when acidified and subsequently neutralised with ammonia, again
develops the red colour of the erythro-salt.

The formation of erythro-ions from methyloximido-oxazolone is shown
by the pink tint of the aqueous solution, which becomes very marked
on warming the solution, but diminishes again on cooling; the colour
is also diminished by the addition of acids, or of alcohol, which would
tend to drive back the dissociation; the substance thus affords an
example of 'ionisation-isomerism' (this vol., i, 400). The increase of
colour is accompanied by an increase of conductivity from $\mu_{32} = 4\cdot1$ at
0° to 11·7 at 25° and 17·5 at 35·5°; the temperature coefficients are
$C_{0°-25°} = 0\cdot0742$ and $C_{0°-35°} = 0\cdot1060$, whilst lævulinic acid, a true acid of
approximately equal strength, gave $C_{0°-25°} = 0\cdot0283$ and $C_{0°-35°} = 0\cdot0277$;
the high temperature-coefficient of the oxazolone, increasing with
rising temperature, is an indication that it is a 'pseudo-acid.' On
the other hand, the conductivity of the red potassium salt is quite
normal; from the values obtained, the dissociation constants of the
oxazolone are calculated to be 0·00080 at 0°, 0·00347 at 25°, and
0·00586 at 35·5°, whilst lævulinic acid gave the values 0·00211, 0·00239,
and 0·00229; the rapid increase of dissociation with temperature is
again an indication of a pseudo-acid. On adding hydrochloric acid to
an equivalent quantity of the red potassium salt, the colour immediately
disappears and the solution has a constant conductivity, showing that
the erythro-ion and the hydrogen ion combine instantly to form the
colourless pseudo-acid; the phenomena of 'gradual neutralisation'
cannot therefore be observed.

Phenyloximido-oxazolone forms a *hydrate* to which the formula
$\text{NOH:C}\diagdown^{\text{C(OH)}_2}_{\text{CPh}\,:\,\text{N}}\diagup\text{O}$, is assigned, but the whole of the water is lost

in 24 hours in a desiccator. It forms a yellow *acid potassium* salt and a violet *neutral potassium* salt; the latter gives a violet solution, which gradually loses its colour, and acquires a smell of bitter almond oil. The *silver* salt is red and explosive. The *methylic* salt separates from light petroleum in yellow crystals and melts at 95—96°; it dissolves in caustic soda to a colourless solution from which the original ether can be recovered by acidifying and extracting with ether. The alcoholic and ethereal solutions of phenyloximido-oxazolone are yellowish, but the aqueous solution has a reddish tint, especially when warm; the appearance of a violet colour on the addition of alkalis is sufficiently sensitive to serve as an indicator for titrating acid and alkali. The conversion of the oxazolone into an open-chain acid is much more rapid than in the previous case, and it is not therefore possible to determine its conductivity; the violet potassium salt has a normal conductivity, and is not hydrolysed at all.

Methylic pseudoviolurate, $CO{<}^{NH \cdot CO}_{NH \cdot CO}{>}C:NOMe$, crystallises from light petroleum in colourless flakes, decomposes at 270°, dissolves in all ordinary solvents, and slightly in water and alkalis, with a pale yellow colour. Violuric acid gives a colourless solution in alcohol, but contrary to the statement of Magnanini, shows a violet colour when dissolved in the purest water, especially on warming. The conductivity also increases with the temperature from $\mu_{32} = 4 \cdot 7$ at 0° to 7·8 at 14·5°, 10·4 at 25°, 13·3 at 35·5°, and 18·8 at 54·1°; the temperature coefficients are $C_{0°-14\cdot5°} = 0 \cdot 0456$, $C_{0°-25°} = 0 \cdot 0485$, $C_{0°-35\cdot5°} = 0 \cdot 0516$, $C_{0°-54\cdot1°} = 0 \cdot 0555$, whilst lævulinic acid gives decreasing values, 0·0297, 0·0293, 0·0277, 0·0249. The dissociation constants are 0·00144 at 0°, 0·00273 at 25°, and 0·00333 at 35·5, whilst lævulinic acid gives 0·00211, 0·00228 and 0·00229. The abnormal temperature coefficients of conductivity and the rapid change in the degree of dissociation show that violuric acid is not a true acid but a pseudo-acid.

Similar phenomena to those described in the paper are also observed with the oximido-imidazolones, $NOH:C{<}^{CO \cdot NH}_{CR = N}{>}$ and the so-called nitroso-hydantoin, $NOH:C{<}^{CO - NH}_{S \cdot C(NH)}{>}$, which also contain the group $-C(NOH) \cdot CO-$, but open-chain compounds such as isonitroso-acetone, $COMe \cdot CH:NOH$, and isonitrosoacetophenone give only yellow salts, and do not show the red to violet tints observed with cyclic oximidoketones. Of the three possible formulæ for the erythro-salts, $^{-C \cdot N \cdot OK}_{-C \cdot O}$, $^{-C = N}_{-C(OK) \cdot O}$, $^{-C \cdot NO}_{-C \cdot OK}$, the second is adopted as the most probable, corresponding with Hantzsch's formula for the erythronitrolic acids. T. M. L.

Narcotine and Narceine. By GEORGE BELL FRANKFORTER and FRANK H. KELLER (*Amer. Chem. J.*, 1899, **22**, 61—67).—Roser (*Annalen*, 1888, **247**, 168) has stated that dimethyltolueneazammonium silver iodide, $C_7H_8Me_2N_3I,2AgI$ (Zincke and Lawson, *Annalen*, 1886, **240**, 128), is formed in converting narcotine into narceine; the compound obtained from narcotine, however, melts at 184—186°,
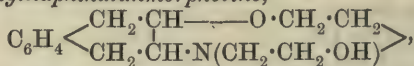
whilst that of Zincke and Lawson melted at 128—130°. The authors' analyses indicate that the substance obtained by Roser, if an azimido-compound, probably has the composition $C_7H_6Me_2N_3Cl,2AgI$.

A better method than that given by Roser for converting narcotine methiodide into the methochloride, and thence into narceine, consists in adding chlorine water to its alcoholic solution; a brown, micro-crystalline precipitate of *di-iodonarcotine methiodide*, $C_{22}H_{21}I_2NO_7,MeI$, is obtained, whilst narcotine methiodide passes into solution, and can be isolated by evaporation. The action apparently takes place nearly quantitatively. Di-iodonarcotine methiodide crystallises from methylic or ethylic alcohol in slender needles, melts at 149°, and is converted by heating with an excess of chlorine water into *di-iodomethylnornar-cotine methiodide*, $C_{20}H_{27}I_2NO_7$, MeI, which crystallises from alcohol in reddish-brown, monoclinic crystals and melts at 186°; in this conversion, it is probable that the methoxyl group which is present in the isoquinoline nucleus remains intact. W. A. D.

Morpholine Bases: Naphthalanmorpholine. By Ludwig Knorr (*Annalen*, 1899, **307**, 171—187. Compare Abstr., 1898, i, 601, and this vol., i, 463).—Naphthalanmorpholine forms prisms which melt at 62—63°, and boils at 312° under 754 mm. pressure; it is not very volatile in steam, and the aqueous solution is strongly alkaline. The *hydrochloride* crystallises in prisms and melts at 275°; the *platinochloride*, *aurichloride*, and *picrate* melt and decompose at 225°, 225°, and 250° respectively. The *nitrosamine* crystallises from absolute alcohol in flattened needles and melts at 161°; the *benzoyl* derivative forms leaflets melting at 194°.

1″-*Hydroxyethylnaphthalanmorpholine*,

$$C_6H_4\begin{cases}CH_2\cdot CH\text{---}O\cdot CH_2\cdot CH_2\\CH_2\cdot CH\cdot N(CH_2\cdot CH_2\cdot OH)\end{cases}\hspace{-1em}\Big\rangle,$$

prepared by heating naphthalanmorpholine with excess of ethylenic oxide at 100°, crystallises from water and from acetone; it melts at 105—108°, and boils at about 300° under 160 mm. pressure. It is likewise produced by the action of hot, 60 per cent. sulphuric acid on dihydroxyethylamidotetrahydro-β-naphthol, $C_6H_4\begin{cases}CH_2\cdot CH\cdot OH\\CH_2\cdot CH\cdot N(CH_2\cdot CH_2\cdot OH)_2\end{cases}$, prepared by heating tetrahydronaphthylene oxide with diethanolamine. The *aurichloride*, *picrolonate*, and *platinochloride* decompose at 213°, 245°, and 235° respectively.

1″-*Methylnaphthalanmorpholine*, obtained from tetrahydronaphthyl-ene oxide and ethanolmethylamine, melts at 57—58° and boils at 317° under 752 mm. pressure; the *hydrochloride* crystallises from alcohol in nodules, and the *platinochloride* forms octahedra or cubes, and melts at 250°, when it decomposes. The *aurichloride* and *picrate* melt at 235° and 206—208° respectively, whilst the *picrolonate* forms a yellow precipitate which dissolves very sparingly in water; the *methiodide* crystallises from water in flattened needles. The aqueous solution of methylnaphthalanmorpholinemethylhydroxide is strongly alkaline, and yields a precipitate with the usual reagents for alkaloids; the *picrate* melts at about 206—208°, the *platinochloride* crystallises in octahedra, and the *aurichloride* in long, flattened needles. On

evaporating a concentrated aqueous solution of the ammonium base, it is resolved into naphthalene and ethanoldimethylamine, the intermediate product being the dihydro-β-naphthol ether of ethanoldimethylamine; this change is analogous to the conversion of codeine into the monomethyl ether of dihydroxyphenanthrene.

$1''$-*Ethylnaphthalanmorpholine*, prepared from tetrahydronaphthalene oxide and ethanolethylamine, boils at 322° under 755 mm. pressure; the *hydrochloride* crystallises from alcohol in prisms and melts at 237—238°. The *picrolonate* and *platinochloride* decompose at 235° and 220° respectively; the *methiodide* dissociates at 205°. M. O. F.

Morpholine Bases of the Camphor Series. By LUDWIG KNORR and PAUL DUDEN (*Annalen*, 1899, **307**, 187—199).—The cyclic bases obtained by intramolecular elimination of water from hydroxyethyl derivatives of amidocamphor and of methylamidocamphor are called *camphenemorpholines* by the authors; reduction adds two atoms of hydrogen, giving rise to *camphanemorpholines*.

Dihydroxyethylamidocamphor, $C_8H_{14}\begin{cases} CH\cdot N(CH_2\cdot CH_2\cdot OH)_2 \\ CO \end{cases}$, prepared by heating amidocamphor with some excess of ethylenic oxide in sealed tubes at 100—110° during 14 hours, is a viscous, brownish oil which dissolves readily in cold, but is sparingly soluble in hot, water; it is only slightly volatile in steam, and reduces Fehling's solution vigorously when heated. The *picrate* crystallises from alcohol in thin, quadratic leaflets and melts at 139—140°, when it decomposes.

Hydroxyethylcamphenemorpholine, $C_8H_{14}\begin{cases} C\text{———}O\cdot CH_2\cdot CH_2 \\ C\cdot N(CH_2\cdot CH_2\cdot OH) \end{cases}$, prepared by heating dihydroxyethylamidocamphor with 40 per cent. sulphuric acid or 20 per cent. hydrochloric acid at 120—130° during 6 hours, is a pale yellow oil which boils at 205—210° and 240° under 70 mm. and 240 mm. pressures respectively; it is indifferent towards Fehling's solution. The *picrate* melts at 127°, and the *hydriodide* crystallises in nacreous leaflets melting at 169—170°.
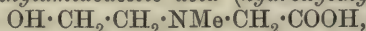
Camphenemorpholine, $C_8H_{14}\begin{cases} C\text{—}O\text{—}CH_2 \\ C\cdot NH\cdot CH_2 \end{cases}$, obtained by heating amidocamphor with 1 mol. of ethylenic oxide, and distilling the crude product under atmospheric pressure, is an alkaline, secondary base which boils at 241—243° under 751 mm. pressure; it has an intense, sweet odour and is indifferent towards hot Fehling's solution. The *picrate* crystallises from alcohol in prisms or pyramids and decomposes at 196—198°.

Methylcamphenemorpholine, $C_8H_{14}\begin{cases} C\text{—}O\text{—}CH_2 \\ C\cdot NMe\cdot CH_2 \end{cases}$, prepared by heating methylamidocamphor with 1 mol. of ethylenic oxide, and distilling the product under atmospheric pressure, boils at 240—241° under 753 mm.; it is indifferent towards Fehling's solution, but the pale yellow base darkens on exposure to air, and exhibits greenish fluorescence. The *picrate* and *platinochloride* decompose at 208° and 204—205° respectively; the *methiodide* crystallises in prisms and melts at 194°.

Methylcamphanemorpholine, $C_8H_{14}\left<\begin{smallmatrix}CH-O-CH_2\\CH\cdot NMe\cdot CH_2\end{smallmatrix}\right.$, obtained by reducing methylcamphenemorpholine with alcohol and sodium, crystallises from petroleum in slender needles, and from water in prisms; it melts at 101° and boils at 252—254°. The *hydrochloride* forms long, slender needles and sublimes when heated, whilst the *hydriodide* decomposes above 250°; the *picrate* melts at 195°, and the *methiodide*, which crystallises from water in lustrous, quadratic leaflets, dissociates at 250° without fusion. The ammonium base yields a *platinochloride* which crystallises from dilute hydrochloric acid in short prisms and decomposes at 127°.   M. O. F.

1 : 3-Methylmorpholone, a Basic δ-Lactone. By LUDWIG KNORR and EDUARD KNORR (*Annalen*, 1899, 307, 199—206. Compare Abstr., 1898, i, 601).—The ready conversion of diethanolamine into morpholine (*loc. cit.*) has suggested the possibility of preparing morpholone, $NH\left<\begin{smallmatrix}CH_2\cdot CH_2\\CH_2-CO\end{smallmatrix}\right>O$, from hydroxyethylamidoacetic acid, but the production of this substance and its transformation into the basic lactone present considerable difficulty; attention has been therefore paid to the methyl derivatives.

Hydroxyethylmethylamidoacetic acid (hydroxyethylsarcosine),
$$OH\cdot CH_2\cdot CH_2\cdot NMe\cdot CH_2\cdot COOH,$$
prepared by heating sarcosine with excess of ethylenic oxide at 80—90° during 24 hours, crystallises in deliquescent needles and melts at 132—133°; the *copper* salt is anhydrous and forms deep blue plates.

1 : 3-Methylmorpholone, $NMe\left<\begin{smallmatrix}CH_2\cdot CH_2\\CH_2-CO\end{smallmatrix}\right>O$, prepared by heating the hydroxy-acid, boils at 233° under 755 mm. pressure; the *hydrochloride* is crystalline, but is exceedingly hygroscopic, and the *picrate* melts at 190—192°. The *methiodide* crystallises from absolute alcohol and decomposes at about 228°; it yields an *aurichloride* which forms slender needles and melts at 205—207°.   M. O. F.

Antipeptone. By MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1899, 27, 335—347). —By the tryptic digestion of proteid, antipeptone is formed. It is not precipitable by ammonium sulphate; it gives a strong biuret, but not Millon's, reaction, and is free from sulphur. In opposition to Kutscher (this vol., i, 179), who regards antipeptone as a mixture of several substances, it is stated that antipeptone of constant composition can be prepared from impure antipeptone by treating it with alcohol. It can also be prepared pure by precipitation with iron salts in a solution saturated with ammonium sulphate.   W. D. H.

Influence of Hydrogen Sulphide on Carbonic Oxide Blood. By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1899, 27, 319—323).—In opposition to Harnack (this vol., i, 467), it is proved that carboxyhæmoglobin is much more resistant to various reagents, including hydrogen sulphide, than is oxyhæmoglobin.   W. D. H.

Organic Chemistry.

Derivatives of Di-isocrotyl and Di-isobutenyl. By S. Pogorželsky (*Chem. Centr.*, 1899, i, 773—775; from *J. Russ. Chem. Soc.*, 1898, **30**, 977—992).—Isobutylene, prepared by the action of alcoholic potash on isobutylic iodide, combines with bromine to form isobutylenic bromide, and this compound, when treated by Butleroff's method (*Krit. Zeit. Chem.*, 1870, 524) yields isocrotylic bromide. This boils at 91—92°, has a sp. gr. 1·3544 at 0° or 1·3254 at 16·5°, and coefficient of expansion 0·00244 between 0° and 16·5°. Di-isocrotyl, prepared by the action of sodium on isocrotylic bromide, boils at 132—134° and melts at 6°. *Di-isocrotylic chloride*,

$$CMe_2Cl \cdot CH_2 \cdot CH_2 \cdot CMe_2Cl,$$
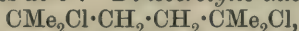
obtained by the action of hydrogen chloride on di-isocrotyl, crystallises in elongated leaflets, melts at 64°, and is soluble in alcohol, ether, benzene, light petroleum, or chloroform; hydrogen chloride is not eliminated by the action of alcoholic potash. *Di-isocrotylic bromide* crystallises in leaflets, melts at 68·5—69°, and is soluble in alcohol, ether, benzene, light petroleum, or chloroform; it is much less stable than the chloride and gradually changes into a dark liquid of penetrating odour. By the action of dilute sulphuric acid (3 vols. acid to 2 vols. water) on di-isocrotyl or of potassium carbonate on di-isocrotylic bromide, di-isocrotylic oxide is obtained; it boils at 113° under 786 mm. pressure, has a sp. gr. 0·8272 at 0° or 0·8113 at 20°, coefficient of expansion 0·000976 between 0° and 20°, and is easily soluble in alcohol, ether, light petroleum, benzene, or chloroform. *Di-isocrotylic bromhydrin*, $CMe_2Br \cdot CH_2 \cdot CH_2 \cdot CMe_2 \cdot OH$, prepared by the action of hydrogen bromide on di-isocrotylic oxide, melts at 77—78°, and, when heated, decomposes into di-isocrotylic bromide and di-isocrotylic oxide. *Di-isocrotylic iodhydrin* is much less stable than the bromhydrin and melts at 70—71°. By the action of dry hydrogen chloride on di-isocrotylic oxide, the dichloride is formed. When the oxide is heated with a 1 per cent. solution of hydrochloric acid at 180—190°, di-isocrotyl is obtained, the unstable glycol,

$$OH \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot CMe_2 \cdot OH,$$
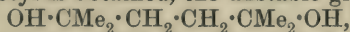
being probably an intermediate product of the reaction. Di-isocrotylic oxide is not affected by heating with water at 190—195°.

Di-isobutenyl, $CH_2 \mathbin{:} CMe \cdot CH_2 \cdot CH_2 \cdot CMe \mathbin{:} CH_2$, prepared by the action of sodium on isobutenylic chloride, boils at 113—114° and when heated with sulphuric acid yields di-isocrotylic oxide, the change in this case being also due to the formation of the unstable glycol. By the action of hydrogen bromide on di-isobutenyl, di-isocrotylic bromide is formed. E. W. W.

Hydrocarbon, $C_{10}H_{18}$, prepared from Active Amylic Alcohol and its Derivatives. By A. Wassiléef (*Chem. Centr.*, 1899, i, 775—776; from *J. Russ. Chem. Soc.*, 1898, **30**, 993—997).—Amylic iodide, prepared from active amylic alcohol, when treated with

potassium hydroxide, yields α-methylethylethylene, $CMeEt:CH_2$, boiling at 31—34°. This readily combines with bromine, forming the bromide, $CMeEtBr \cdot CH_2Br$, which has a sp. gr. 1·6921 at 0° and 1·6638 at 21°. *β-Brom-α-methylethylethylene*, $CMeEt:CHBr$, obtained by the action of alcoholic potash on the bromide, boils at 117—118° under 767·7 mm. pressure, and has a sp. gr. 1·2668 at 0° and 1·2423 at 20°. A *hydrocarbon*, $C_{10}H_{18}$, is obtained by treating the bromamylene with sodium ; it boils at 167—170°, and by the action of dilute sulphuric acid (3 vols. of acid to 1 of water) forms the corresponding ditertiary-γ-oxide,

$$\begin{matrix} CMeEt \cdot CH_2 \\ | \\ CMeEt \cdot CH_2 \end{matrix} \Big> O,$$ probably by means of the intermediate production

of the glycol. The oxide boils at 159—161°, has a pleasant, camphor-like odour, and, by the action of hydrogen bromide dissolved in light petroleum, yields a compound, $C_{10}H_{20}Br_2$. E. W. W.

Action of Zinc Dust on Alcoholic Solutions of α-Halogen-substituted Alcohols and of Zinc Shavings on Alcoholic Solutions of their Acetates. By Živoin Jocitsch and Alexei Faworsky (*Chem. Centr.*, 1899, i, 777—778 ; from *J. Russ. Chem. Soc.*, 1898, 30, 998—1003. Compare this vol., i, 748, and Mokiewsky, this vol., i, 729).—The best yields of α-dihalogen-substituted ethylenes are obtained by treating the alcoholic solutions of the acetates of α-trihalogen-substituted alcohols with zinc shavings. Under these conditions, trichlorethylic acetate, $COMe \cdot OCH_2 \cdot CCl_3$, forms unsymmetrical dichlorethylene, $CCl_2:CH_2$, and a small quantity of a gas which combines with bromine, and is probably chlorovinyl. Trichloropropylic acetate, $COMe \cdot OCHMe \cdot CCl_3$, yields α-dichloropropylene, $CCl_2:CHMe$, which boils at 76·5°, has a sp. gr. 1·2030 at 0°/0° and 1·1764 at 19·5°/0°. Acetonechloroform acetate, $COMe \cdot OCMe_2 \cdot CCl_3$, gives 85 per cent. of α-dichlorisobutylene, $CCl_2:CMe_2$, which boils at 107·5—108·5°, and has a sp. gr. 1·1697 at 0°/0° and 1·1449 at 20°/0°. Trichloromethylphenyl-carbinol acetate, $COMe \cdot O \cdot CHPh \cdot CCl_3$, yields 90 per cent. of dichloro-styrene, which boils at 220—222°, has a sp. gr. 1·2678 at 0°/0° and 1·2499 at 19°/0°, and tribromomethylphenylcarbinol acetate gives monobromostyrene, $CHBr:CHPh$, which boils at 218—220° and has a sp. gr. 1·4482 at 0°/0° and 1·4289 at 19°/0°. E. W. W.

Purification and Preservation of Chloroform. By V. Masson (*J. Pharm.*, 1899, [vi], 9, 568—572).—Methods are described for the purification and preservation of chloroform for anæsthetic purposes. Poppy seed oil possesses in a remarkable degree the property of preventing pure chloroform from undergoing any change. A specimen of pure chloroform which contained 1 part of the oil in 1000 parts, and had been exposed to both diffused light and direct sunlight, remained quite pure for 3 years. H. R. Le S.

Action of Bromine on Isobutylic Bromide in presence of Aluminium Bromide and Chloride. By A. Mouneyrat (*Compt. rend.*, 1899, 129, 226—228).—When bromine acts on isobutylic bromide in presence of aluminium bromide, the products are (1) a small quantity of isobutylenic bromide, (2) a large quantity of the tribromisobutane, $CMe_2Br \cdot CHBr_2$, a colourless liquid of sp. gr. 2·188 at 16°, which boils

at 110—114° under 15 mm. pressure, (3) small quantities of an isomeric tribromisobutane, and a tetrabromisobutane. No variations in the relative proportions of isobutylic bromide and bromine led to a satisfactory yield of isobutylenic bromide. If, however, a small quantity of aluminium chloride is used instead of the bromide, the isobutylenic bromide, $CMe_2Br \cdot CH_2Br$, which boils and decomposes at 148—149° under normal pressure, is obtained in quantity amounting to 50—55 per cent. of the calculated yield.

Tribromisobutane, $CMe_2Br \cdot CHBr_2$, when treated with bromine in presence of aluminium chloride or bromide, yields 65—70 per cent. of the theoretical yield of tetrabromisobutane, $CH_2Br \cdot CMeBr \cdot CHBr_2$; this has a sp. gr. 2·557 at 16°, and boils at 159—163° under 12 mm. pressure.   C. H. B.

Action of Sulphuric Acid on Nitroheptane. By R. A. Worstall (*Amer. Chem. J.*, 1899, 22, 164—167).—When nitroheptane is heated with dilute sulphuric acid at 80° for 10 minutes, or is gradually mixed with an excess of concentrated sulphuric acid (sp. gr. 1·84) at the ordinary temperature, it is converted into heptoic acid, but when added to five times its weight of well-cooled, fuming sulphuric acid, there is formed, in addition to heptoic acid, a small quantity of *nitroheptanesulphonic acid*, the *barium* salt, $(NO_2 \cdot C_7H_{14} \cdot SO_3)_2Ba$, of which is easily soluble in water and in hot alcohol, and crystallises from the latter in small plates.   W. A. D

A Colour Reaction of Vinylic Alcohol. By ENRICO RIMINI (*Gazzetta*, 1899, 29, i, 390—393).—After shaking cheese with concentrated hydrochloric acid to dissolve the casein, gentle heating and shaking with a few drops of ether in some cases produces an azure-violet coloration, the intensity of which varies with the sample of ether employed; pure ether, recently distilled over lime and sodium, gives no colour. The author finds that the formation of this colour is due to the presence of vinylic alcohol in the ether. Further, Liebermann's reaction for proteids, namely, the production of an azure-violet, when the proteid, after boiling with alcohol and washing with ether, is heated with concentrated hydrochloric acid, fails if ether containing no vinylic alcohol is employed.   T. H. P.

Oxidation of Propylenic Glycol by Bromine Water. By ANDRÉ KLING (*Compt. rend.*, 1899, 129, 219—220).—Acetol, $CH_3 \cdot CO \cdot CH_2OH$, is formed when propylenic glycol is mixed with a molecular proportion of bromine dissolved in water and the mixture is exposed to sunlight.   C. H. B.

Formation of a Sugar from Egg Albumin. By PAUL MAYER (*Chem. Centr.*, 1899, i, 687; from *Deutsch. Med. Woch.*, 25, 95—97). —Egg albumin was prepared in the form of a white powder, free from glucose, by removing the fat from yolk of egg by means of ether, and then treating with water and alcohol. By boiling this substance with a 4—5 per cent. solution of hydrochloric acid for 6 hours according to Krawkow's method (*Pflüg. Arch.*, 65, 281), a carbohydrate was obtained, which dissolved in glacial acetic acid, forming a lævo-

rotatory solution and yielded an osazone melting at 203°. Analysis showed it to be a hexose, and the properties of its osazone are identical with those of glucosazone.   E. W. W.

Colour Reactions of Oxycellulose. By EDMOND JANDRIER (*Compt. rend.*, 1899, **128**, 1407—1408).—The oxycelluloses, and especially that obtained by the oxidation of cotton with potassium chlorate (Vignon's process), yield colour reactions when a solution or suspension is mixed with a phenol, and concentrated sulphuric acid is added so that it forms a layer below the organic mixture ; the coloration is developed at the junction of the liquids. A golden yellow is produced with phenol ; varying shades of violet are obtained with α-naphthol, menthol, thymol, and the alkaloids morphine and codeine ; β-naphthol, quinol, and resorcinol give brown shades, and gallic acid gives a green coloration at the junction, which changes to violet in the sulphuric acid. Formaldehyde, gum arabic, and the aldoses give colour reactions when similarly treated.   G. T. M.

Nitromalonic Aldehyde. By HENRY B. HILL and JOSEPH TORREY, jun. (*Amer. Chem. J.*, 1899, **22**, 89—110).—The authors find that the colourless compounds, $C_3H_2NO_4K + H_2O$ and $C_3H_2NO_4Na + H_2O$, obtained respectively as final products of the action of potassium and sodium nitrite on mucobromic acid (Hill and Sanger, Abstr., 1883, 47), are salts of *nitromalonic aldehyde*, $CHO \cdot CH(NO_2) \cdot CHO$. This aldehyde, obtained by adding an ethereal solution of hydrogen chloride to the silver salt suspended in absolute ether, crystallises from light petroleum in feathery aggregates of prisms and melts at 50—51° ; its molecular weight was determined cryoscopically, using benzene as the solvent. In aqueous solutions, it is slowly decomposed at the ordinary temperature, more rapidly at 45—50°, giving rise to 1 : 3 : 5-trinitrobenzene and formic acid. The *anil*, $C_3H_3NO_3$:NPh, obtained on adding aniline hydrochloride to an aqueous solution of the sodium salt, crystallises from alcohol in lustrous, yellow scales, and melts at 143—144° ; if aniline is employed instead of its hydrochloride, the *dianil*, $C_3H_3NO_2(NPh)_2$, is obtained in the form of brilliant yellow needles. The *paratolils*, $C_{10}H_{10}N_2O_3$, and $C_{17}H_{17}N_3O_2$, prepared similarly from paratoluidine, melt respectively at 176—177° and 138°.

The *phenylhydrazone*, $C_9H_9N_3O_3$, formed on adding phenylhydrazine hydrochloride to a solution of sodium nitromalonic aldehyde, forms yellow needles and melts and decomposes at about 101° ; the *diphenylhydrazone*, $C_{15}H_{15}N_5O_2$, obtained by adding dilute alcoholic phenylhydrazine to the sodium derivative of the aldehyde and passing carbonic anhydride through the solution, is a dark-red, unstable, crystalline substance which melts and decomposes at about 98°, and yields a stable, crystalline *sodium* derivative, $C_{15}H_{14}N_5O_2Na$, and a *lead* salt, $(C_{15}H_{14}N_5O_2)_2Pb$. When either of the phenylhydrazones is heated, alone or with alcohol, 1-*phenyl-4-nitropyrazole*,

$$\begin{array}{c} CH\!=\!\!=\!\!=\!N \\ | \qquad\qquad \diagdown NPh, \\ C(NO_2)\!:\!CH \end{array}$$
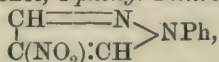
is obtained ; this crystallises from alcohol in slender, slightly coloured, prismatic clusters, from light petroleum in white, silky needles, and

melts at 126—127°. 4-Nitropyrazole (Buchner and Fritsch, Abstr., 1893, i, 432; and Knorr, *Annalen*, 1894, **279**, 228) is obtained when the product of the action of hydrazine sulphate (2 mols.) on nitromalonic aldehyde is heated with moderately concentrated hydrochloric acid; this melted at 157—158° (162° corr.) and its production affords a proof of the structure of the aldehyde.

β-Nitroisoxazole, $C_3H_2N_2O_3$, formed on adding hydroxylamine hydrochloride (1 mol.) to concentrated, aqueous sodium nitromalonic aldehyde, crystallises from a mixture of ether and light petroleum in aggregates of transparent, rhombic plates, and melts at 46—47°; if this action is carried out in presence of an equivalent quantity of sodium carbonate or sodium hydroxide, transparent, yellow crystals of the *sodium* derivative, $C_3H_4N_3O_4Na$, of *nitromalonic dialdoxime* are obtained; the corresponding *silver* salt, $C_3H_4N_3O_4Ag$, is a pale yellow, microcrystalline powder; the dioxime could not be isolated. *Nitromalonic aldehyde aniloxime*, $NPh{:}CH{\cdot}CH(NO_2){\cdot}CH{:}N{\cdot}OH$, formed on adding aniline hydrochloride to a solution of the sodium derivative of the dioxime, crystallises from alcohol in yellow, globular aggregates, and melts at 162°; it can also be obtained by acting with hydroxylamine on the monanil of nitromalonic aldehyde (m. p. 143—144°).

In alkaline solution, nitromalonic aldehyde readily condenses with acetone to form paranitrophenol, and similar condensation products are formed with ketonic acids and other ketones.   W. A. D.

Azelaone. By W. MILLER and A. TSCHITSCHKIN (*Annalen*, 1899, **307**, 375—383. Compare Mager, Abstr., 1893, i, 558, and Derlon, Abstr., 1898, i, 638).—The best yield of azelaone is obtained when small quantities of azelaic acid are distilled with an equal weight of soda lime; it boils at about 205°. The gaseous products of the distillation, when passed through bromine, formed erythrene tetrabromide, $CH_2Br{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br$, together with ethylenic and propylenic dibromides.   M. O. F.

Acetylacetonates [Metallic Derivatives of Acetylacetone]. By G. URBAIN and A. DEBIERNE (*Compt. rend.*, 1899, **129**, 302—305. Compare Abstr., 1897, i, 236).—The compounds of acetylacetone with the sesquioxides crystallise in similar forms, melt without decomposition, and are more or less volatile; when crystallised from chloroform, they all retain 2 mols. of the solvent; their molecular weights, determined by cryoscopic methods, correspond with those required for the simple formula $R(CHAc_2)_3$.

The *ferric* derivative, $Fe(CHAc_2)_3$, prepared by digesting ferric hydroxide with excess of acetylacetone, forms a bright red, crystalline precipitate almost insoluble in water; it is soluble in the ordinary organic solvents, can be crystallised from benzene and melts at 184°. The *manganic* derivative crystallises from ether in shining, black crystals and melts at 172°. The *cobaltic* derivative melts at 240°, and is more stable than the preceding salts; its solutions in organic solvents are intensely green, and it separates from these in black crystals. The *chromic* derivative is a reddish-violet salt melting at 214° and boiling at 340° without decomposition; the vapour is green.

The *aluminic* derivative cannot be easily obtained from the hydroxide; it is, however, readily prepared from the anhydrous chloride. The *nickelic* derivative could not be isolated.

<div align="right">G. T. M.</div>

Dichlorobutyric Acid (Dichloro-3 : 4-butanoic Acid). By ROBERT LESPIEAU (*Compt. rend.*, 1899, **129**, 224—225).—The chloronitrile obtained by the action of potassium cyanide on epichlorhydrin (this vol., i, 243) yields crotonic acid (m. p. 72°) on careful reduction with hydriodic acid; it therefore has the constitution

$$CH_2Cl \cdot CH(OH) \cdot CH_2 \cdot CN.$$
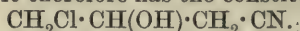
When treated with phosphorus pentachloride, it yields a *dichloronitrile*, $CH_2Cl \cdot CHCl \cdot CH_2 \cdot CN$, which boils at 113—114° under 25 mm. pressure, and has a sp. gr. 1·314 at 0°. *βγ-Dichlorobutyric acid*, $CH_2Cl \cdot CHCl \cdot CH_2 \cdot COOH$, obtained from the nitrile by hydrolysis, melts at 49—50°; its *ethylic* salt boils at 206—209° under 750 mm., and at 92° under 14 mm. pressure.

<div align="right">C. H. B.</div>

Identification and Separation of Fatty Acids by means of Tetrachloroquinol. By LOUIS BOUVEAULT (*Compt. rend.*, 1899, **129**, 53—56).—The identification and separation of the fatty acids by means of the compounds which they form with tetrachloroquinol is attended with considerable advantages, the amides, anilides, paratoluidides, and phenylhydrazides, which have been used for these purposes, being in many cases difficult to purify, whilst the regeneration of the acids therefrom is often very troublesome. When tetrachloroquinol is heated in a reflux apparatus with excess of an acid chloride, $R \cdot CO \cdot Cl$, it reacts with 1 and 2 mols. of the latter to form monacid and diacid derivatives respectively. The di-acid derivatives, $C_6Cl_4(O \cdot CO \cdot R)_2$, are very soluble in ether, benzene, chloroform, hot methylic or ethylic alcohols, but less so in light petroleum, and insoluble in water. They are stable, well crystallised substances, which are not acted on by dilute acids and alkalis; warm alcoholic potash rapidly hydrolyses them with regeneration of the acid. The monacid derivatives, $OH \cdot C_6Cl_4 \cdot O \cdot CO \cdot R$, are also well crystallised, and are distinguished from the preceding compounds by their solubility in dilute alkalis; they are also more soluble in alcohol, and less soluble in light petroleum than the di-acid derivatives. The di-acid derivatives of acetic (245°), propionic (160°), butyric (137°), and α-dimethylisocrotonic (130—134°) acids have the melting points indicated; the monacid derivative of the last named acid melts at 132°.

<div align="right">N. L.</div>

Action of Pyruvic Acid on Malonic Acid : Synthesis of Itaconic Acid. By KARL GARZAROLLI-THURNLACKH (*Monatsh.*, 1899, **20**, 467—479).—When pyruvic and malonic acids, in molecular proportion, are dissolved in glacial acetic acid and the solution is warmed on a water-bath until carbonic anhydride is no longer evolved, itaconic and citramalic acids are obtained, the former being the principal product. A third acid, isomeric with citramalic acid, also seems to be produced, but no evidence was obtained of the formation of citraconic acid in the reaction. The production of itaconic to the exclusion of citraconic acid makes it probable that pyruvic acid reacts in the enolic

form. It is noteworthy, therefore, that, contrary to Schiff's statement (Abstr., 1898, i, 490), the pyruvic acid used, and also its condensation product with benzylideneaniline, gave a coloration with an ethereal solution of ferric chloride. R. H. P.

Ethylic Azelate. By W. MILLER (*Annalen*, 1899, **307**, 384—386). —*Ethylic azelate* is a colourless, somewhat viscous liquid, having a slight, agreeable odour, and distilling at 291—292°; its sp. gr. is 0·9906 at 0°/0° and 0·9766 at 15°/0°. M. O. F.

Methylic Hydroxymethylenecyanacetate and some of its Homologues. By E. GRÉGOIRE DE BOLLEMONT (*Compt. rend.*, 1899, **129**, 50—53).—According to Claisen (Abstr., 1897, i, 592), hydroxymethylene derivatives of the type of ethylic hydroxymethyleneacetoacetate may be regarded as formic acid in which oxygen has been replaced by a carbon atom united to two negative groups. Such compounds behave, in fact, like strong monobasic acids, and the introduction of a more negative radicle, such as cyanogen, in place of the acetyl group might be expected to lead to the formation of compounds of a still more pronouncedly acid character. The alkylic hydroxymethylenecyanacetates, obtained by hydrolysis of the corresponding methoxy- and ethoxy-methylenecyanacetates (Abstr., 1899, i, 736), have properties which show that this is the case. These compounds are strong monobasic acids which displace carbonic and acetic acids from their salts, and are converted by the action of ammonia and aniline into the corresponding amido- and anilido-methylenecyanacetates. They are slightly soluble in water, more soluble in alcohol and ether, and undergo more or less decomposition when distilled under diminished pressure. Their aqueous solutions give an intense orange-brown coloration with ferric chloride.

Methylic hydroxymethylenecyanacetate, $OH\cdot CH\colon C(CN)\cdot COOMe$, is a crystalline substance of pungent odour and melts at 136—137°. The value found for its affinity coefficient ($K = 1·505$) shows that it may be compared with the chloracetic acids. The *barium* salt crystallises with $1H_2O$ and is soluble in hot water, but only slightly so in alcohol or ether; it becomes anhydrous at 150° and at the same time acquires a yellowish tint. The *copper* salt, with $2H_2O$, forms pale green crystals, which become anhydrous and darken in colour at 110°. The *silver* salt crystallises in silky tufts and is converted by the action of methylic iodide into methylic methoxymethylenecyanacetate. *Ethylic hydroxymethylenecyanacetate*, $OH\cdot CH\colon C(CN)\cdot COOEt$, was obtained as a colourless oil, and also in the form of transparent plates melting at 68—69°. *Amylic hydroxymethylenecyanacetate* could only be obtained in an impure state as an uncrystallisable oil. N. L.

Conversion of Alkylic Dibromacetoacetates into Mesaconic Acid and its Homologues. By W. SSEMENOFF (*Chem. Centr.*, 1899, i, 781—784; from *J. Russ. Chem. Soc.*, 1898, **30**, 1009—1030).—The paper contains a criticism of the various theories of the mechanism of the reaction whereby alkylic dibromacetoacetates are converted into mesaconic acid and its homologues. By boiling ethylic methyl-

acetoacetate with bromine (2 mols.) and water as long as carbonic anhydride is evolved, an oil containing mono-, di-, and tri-bromo-methyl ethyl ketone is obtained. By heating this oil with a 10 per cent. solution of sodium carbonate and acidifying the product, isocrotonic acid, or probably a mixture of this acid with crotonic acid, is formed. According to Faworsky's first theory of the method of formation of unsaturated acids from dichloroketones, a-bromobutyric acid should be the first product of the above reaction, but by the action of sodium carbonate this acid forms a-hydroxybutyric acid, and not isocrotonic acid. Faworsky's second theory is adopted by the author, and the conversion of alkylic dibromacetoacetates into mesaconic acid is represented as follows : $CHBr_2 \cdot C(OH) \vdots CMe \cdot COOEt - HBr =$

$$O < \begin{matrix} CHBr \\ | \\ CMe \cdot COOEt \end{matrix} = COBr \cdot CH \vdots CMe \cdot COOEt.$$
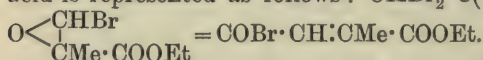
The intermediate unstable oxide and the acid bromide cannot be isolated, but by the action of an alcoholic instead of an aqueous solution of an alkali carbonate, the ethoxy-compound corresponding with the acid bromide may be obtained if the action is stopped before the alkali hydroxide has completely hydrolysed it. These ethoxy-compounds are also formed in large quantities by the action of alcoholic potash on alkylic dibromalkylacetoacetates at a low temperature, and may be removed by distilling in steam.

The neutral compound obtained in the preparation of dimethyl-mesaconic acid from ethylic dibromisopropylacetoacetate boils at 240—241°, and consists mainly of diethylic dimethylmesaconate, whilst that formed in the preparation of ethylmesaconic acid from ethylic dibromopropylacetoacetate is diethylic ethylmesaconate. By the action of alcoholic potash on ethylic dibromethylacetoacetate, an oil is formed which, when hydrolysed, yields methylmesaconic acid, and when only 2 mols. of potassium hydroxide are used, this compound is the main product of the reaction. According to the author, the boiling point of Faworsky's dichloroketone, $COMe \cdot CCl_2 \cdot CH_2Me$, indicates that it probably contained the compound $CMeCl_2 \cdot CO \cdot CH_2Me$ to some extent, and this would explain the formation of both angelic and a-ethylacrylic acids.

By the action of alcoholic potash on alkylic dibromalkylaceto-acetates, small quantities of bye-products containing easily volatile acids which decolorise potassium permanganate are obtained ; these probably result from the decomposition of ketones formed by the action of hydrogen bromide. In the case of ethylic dibromethyl-acetoacetate, propylideneacetic and butyric acids were identified. These syrupy acid liquids, when distilled, yield two fractions of which the one insoluble in water contains ethylic mesaconate or homologous compounds, whilst the fraction soluble in water, when distilled with steam, yields acids which are not easily volatile and are not hydroxy-acids.

By the action of an aqueous solution of potassium carbonate on ethylic dibromacetosuccinate, an acid, which is probably aconitic acid, is practically the only product, whilst by the action of an alcoholic solution of potassium hydroxide, the following at least are formed :

fumaric acid, a dimorphous, crystalline acid which melts at 185—190°, aconitic acid, and a syrupy acid. E. W. W.

Synthesis of Lævulinic Acid. By EDMOND E. BLAISE (*Bull. Soc. Chim.*, 1899, [iii], **21**, 647—650. Compare this vol., i, 331).— Carbethoxypropionic chloride, $COOEt \cdot CH_2 \cdot CH_2 \cdot COCl$, reacts with zinc methyl in benzene solution to form ethylic lævulinate. The *semicarbazone*, $NH_2 \cdot CO \cdot NH \cdot ON:CMe \cdot CH_2 \cdot CH_2 \cdot COOH$, obtained from lævulinic acid, crystallises from boiling alcohol in slender needles melting at 187°. N. L.

Homologues of Mesaconic, Citraconic, and Itaconic Acids. By W. SSEMENOFF (*Chem. Centr.*, 1899, i, 780—781; from *J. Russ. Chem. Soc.*, 1898, **30**, 1003—1009. Compare *J. Russ. Chem. Soc.*, **23**, 430). —A yield of 35—40 per cent. of dimethylmesaconic acid (Demarçay's oxyisohexinic acid) is obtained by decomposing ethylic dibromiso-propylacetoacetate with sufficient alcoholic potash to render the mass permanently alkaline. The acid is purified by converting it into the diethylic salt which boils at 239—240°, and is easily hydrolysed by alkalis, but only partially by a 50 per cent. solution of sulphuric acid. The acid melts at 186°; the calcium salt, $C_7H_8O_4Ca + 2H_2O$, crystallises from water in small prisms, and the silver salt, $C_7H_8O_4Ag_2$, in needles.

Dimethylcitraconic anhydride, prepared by heating dimethyl-mesaconic acid with acetic chloride (2 mols.) at 110°, boils at 138° under 61 mm. pressure, melts at 5·25°, has a sp. gr. 1·1425 at 0°/0°, and dissolves easily in water, forming a solution which decomposes car-bonates and, when evaporated, yields the original anhydride. Calcium dimethylcitraconate, $C_7H_8O_4Ca + H_2O$, crystallises from water in plates, and the barium salt, $C_7H_8O_4Ba + 1\frac{1}{2}H_2O$, in small plates; the silver salt forms a powder and is very sparingly soluble in water.

Dimethylitaconic acid, obtained by heating dimethylcitraconic anhydride with 2—3 times its volume of water at 140°, crystallises from water in long prisms and from alcohol in thin, pointed plates, and melts at 154—156°. Teraconic acid, which must be identical with this acid, melts at 161—163°; when heated, however, at the rate of 4° per minute, it melts at 154—156°. Both acids, when heated with a 50 per cent. solution of sulphuric acid, yield terebic acid melting at 174—175°, and both form anhydrous barium salts.

When dimethylcitraconic anhydride or dimethylitaconic acid is heated with water at 190°, carbonic anhydride is liberated and isocaprolactone, $\begin{smallmatrix} CH_2 \cdot CMe_2 \\ | \\ CH_2 \!-\!\!-\! CO \end{smallmatrix}\!\!>\!\!O$, is formed. The lactone is a neutral oil, boils at 205—206° under 753 mm. pressure, and, when warmed with baryta water, forms an amorphous barium salt which, with silver nitrate, yields silver hydroxyisocaproate. Terebic acid, when distilled with a 50 per cent. solution of sulphuric acid, forms capro-lactone, hence the formation of the latter from dimethylitaconic acid might easily depend on its conversion into terebic acid, but no trace of terebic acid was found in the acid mother liquor. By heating dimethylitaconic acid with a 20 per cent. solution of sulphuric acid at

175° for 24 hours, caprolactone is obtained and ethylmesaconic acid under similar conditions also yields a lactone-like oil.   E. W. W.

Ethylic Glutaconate, I. By FERDINAND HENRICH (*Monatsh.*, 1899, **20**, 539—569).—The hydrogen of the methylene group of ethylic glutaconate, $COOEt \cdot CH\!:\!CH \cdot CH_2 \cdot COOEt$, is displaceable by alkyl radicles, owing to the influence of the adjacent $\cdot CO \cdot$ and $\cdot CH\!:\!CH \cdot$ groups, and in this respect the compound resembles resorcinol, the diketonic formula for which also contains the $\cdot CH\!:\!CH \cdot CH_2 \cdot CO \cdot$ group (Herzig and Zeisel, Abstr., 1890, 1404); the substitution, however, takes place much more readily in the glutaconate, both hydrogen atoms being displaced.

Ethylic glutaconate has a sp. gr. 1·0499 at 20°/4°; the index of refraction for sodium light is n_D 1·4474; the molecular refraction is 47·27, using the formula of Lorenz and Lorentz, the calculated value being 46·87; the molecular weight, determined from the freezing point of a solution in benzene, is normal. It is hydrolysed by boiling with caustic soda, or by warming with sodium ethoxide in alcoholic solution; the *sodium* derivative, $COOEt \cdot CH\!:\!CH \cdot CHNa \cdot COOEt$, however, is precipitated as a yellow salt when dry ether is added to a freshly-prepared solution of the substance in alcoholic sodium ethoxide. It is readily oxidised by potassium permanganate, and seems to give no characteristic coloration with alcoholic or ethereal ferric chloride, although on one occasion a very pure specimen, after solution in alcoholic sodium ethoxide and precipitation with dilute sulphuric acid, gave an intense red-violet coloration.

Methylic iodide acts very vigorously on a solution of ethylic glutaconate in alcoholic sodium ethoxide; the monomethyl derivative was not isolated, but by hydrolysis of the product a mixture of acids was obtained, of which a fraction melting at 118—130° seemed to consist chiefly of monomethylglutaconic acid. *Dimethylglutaconic acid* sinters at 123° and melts at 129—130°, although it only becomes transparent at 132—133°; it dissolves readily in cold ether, alcohol, or acetic acid, less readily in benzene, toluene, chloroform, or light petroleum, and crystallises from water in beautiful, snow-white forms. It is not acted on by nitrous acid, but is oxidised by potassium permanganate, yielding dimethylmalonic acid. An amorphous substance, insoluble in toluene, was also produced in the preparation of dimethylglutaconic acid; this melted at 171—172°, with decomposition, contained $C = 48·55$, $H = 5·26$ per cent., and was not acted on by potassium permanganate.

Ethylic isonitrosoglutaconate, $COOEt \cdot CH\!:\!CH \cdot C(NOH) \cdot COOEt$, prepared by the action of nitrous acid on ethylic sodioglutaconate, melts at 81—83°, crystallises from light petroleum in white needles, dissolves readily in cold benzene, chloroform, or acetone, and moderately in alcohol or acetic acid. It is strongly acid, decomposes carbonates, is soluble in alkalis with an intense yellow coloration, dissolves in hot, but not in cold, concentrated hydrochloric acid, and reduces Fehling's solution.

Phenylazoglutaconic acid, $COOH \cdot CH\!:\!CH \cdot CH(COOH) \cdot N\!:\!NPh$ or $COOH \cdot CH \cdot CH \cdot C(COOH)\!:\!N \cdot NHPh$, melts at 162·5° with evolution of

gas, dissolves readily in hot, and moderately in cold alcohol, but only slightly in ether, alcohol, or acetone, or in hot benzene or chloroform, and is insoluble in light petroleum. In concentrated sulphuric acid, it forms a dark, reddish-yellow solution. The *monethylic* salt crystallises from dilute alcohol in yellow needles, melts and decomposes at 152—153°, dissolves readily in ether, chloroform, or alcohol, less readily in acetic acid, and only slightly in benzene or light petroleum ; it dissolves in sulphuric acid with a reddish-yellow coloration, and gives a transient blue coloration with potassium dichromate, ferric chloride, or sodium nitrite.

Ethylic glutaconate condenses with benzaldehyde and acetaldehyde, but definite products were not isolated. T. M. L.

Direct Conversion of Acetamide into Ethylamine by Reduction. By GUERBET (*Compt. rend.*, 1899, **129**, 61—63).—When a solution of acetamide in amylic alcohol is boiled in a reflux apparatus with metallic sodium, one half of the acetamide is converted into ethylamine, whilst the other half is decomposed, with formation of ammonia, by the sodium hydroxide produced in the first reaction.

N. L.

Ureides and Acylated Alkylic Carbamates. By HEINRICH BECKURTS (*Arch. Pharm.*, 1899, **237**, 285—288).—An introduction to the two following papers. C. F. B.

Action of Alkylsulphinates on Chloracetylurethanes and Chloracetocarbamides. By G. FRERICHS (*Arch. Pharm.*, 1899, **237**, 288—299). — By heating together chloracetic chloride, $CH_2Cl \cdot COCl$, and a urethane, $NH_2 \cdot CO \cdot OR$ [R = Et, iso-Bu, Ay], and crystallising the product from alcohol, a chloracetylurethane, $COOR \cdot NH \cdot CO \cdot CH_2Cl$, is obtained. When this is heated with a sulphinate, $R' \cdot SO_2Na$ [R' = Ph, paratolyl], in alcoholic solution, a sulphonacetylurethane, $COOR \cdot NH \cdot CO \cdot CH_2 \cdot SO_2 \cdot R'$, is formed. This is decomposed when heated with aqueous caustic soda into carbonic anhydride, the alcohol $R \cdot OH$, ammonia, and the sulphonacetic acid, $SO_2R' \cdot CH_2 \cdot COOH$; no doubt the first three substances result from the further action of the alkali on the urethane, $COOR \cdot NH_2$, first eliminated. With alcoholic caustic potash in the cold, the products are the sulphonacetic acid and the urethane, but, on boiling, these undergo further decomposition, in this case into the sulphone $R' \cdot SO_2 \cdot CH_3$ and carbonic anhydride, and into carbonic anhydride, the alcohol $R \cdot OH$, and ammonia respectively. The compounds prepared, and their melting points, are as follows : *Chloracetylethylurethane,* 129° ; *phenylsulphonacetylethylurethane,* 69° ; *paratolylsulphonacetylethylurethane,* 103° ; *chloracetylisobutylurethane,* 72° ; *phenylsulphonacetylisobutylurethane,* 81° ; *paratolylsulphonacetylisobutylurethane,* 89° ; *chloracetylamylurethane,* 68° ; *phenylsulphonacetylamylurethane,* 73·5° ; *paratolylsulphonacetylamylurethane,* 83°.

By heating chloracetic chloride with a carbamide, for example, methylcarbamide, $NHMe \cdot CO \cdot NH_2$, a chloracetylcarbamide,
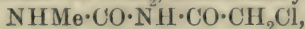
$$NHMe \cdot CO \cdot NH \cdot CO \cdot CH_2Cl,$$

is obtained. This reacts with sulphinates as the chloracetylurethanes do,

and yields sulphonacetylcarbamides, $NHMe\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot SO_2R'$. These are decomposed by alcoholic potash much in the same way as the analogous urethane derivatives; paratolylsulphonacetylmethyl-carbamide, for example, yields methylcarbamide and paratolylsulphon-acetic acid, or eventually methylamine, ammonia, carbonic anhydride, and paratolylmethylsulphone. The following are the compounds prepared: *Phenylsulphonacetylcarbamide*, 225°; *paratolylsulphonacetyl-carbamide*, 223—224°. *Chloracetylmethylcarbamide*, 205°; *phenyl-sulphonacetylmethylcarbamide*, 207°; *paratolylsulphonacetylmethylcarb-amide*, 220°.   C. F. B.

Action of Potassium Hydrosulphide and Thiocyanate on Chloracetylurethanes and Chloracetocarbamides. By G. FRERICHS (*Arch. Pharm.*, 1899, **237**, 300—331).—When a chloracetyl-urethane, $COOR\cdot NH\cdot CO\cdot CH_2Cl$ [R = Et, iso-Bu, Ay], is dissolved in warm alcohol and alcoholic potassium hydrosulphide is added gradually until excess is present, potassium chloride is deposited, hydrogen sulphide is evolved, and on pouring the mixture into water a thio-di-glycolylurethane, $(COOR\cdot NH\cdot CO\cdot CH_2)_2S$, separates; it was not found possible to obtain compounds of the type $COOR\cdot NH\cdot CO\cdot CH_2\cdot SH$. *Thiodiglycolyl-diethyl-, -di-isobutyl-*, and *-diamyl-urethanes* melt at 187°, 127°, and 137·5° respectively.

Potassium hydrosulphide reacts in a similar manner with chloraceto-carbamides, for example, with $NHMe\cdot CO\cdot NH\cdot CO\cdot CH_2Cl$, yielding thiodiglycolylcarbamides, $(NHMe\cdot CO\cdot NH\cdot CO\cdot CH_2)_2S$. *Thiodiglycolyl-carbamide* and *-dimethylcarbamide* are amorphous and decompose with-out melting when heated.

When chloracetylethylurethane is heated for a few minutes on the water-bath with potassium thiocyanate in alcoholic solution, and cold water is added gradually to the filtered solution, *thiocarbimidoacetyl-ethylurethane*, $COOEt\cdot NH\cdot CO\cdot CH_2\cdot NCS$, separates; this melts at 86° and dissolves in hot aqueous caustic soda, yielding a red solution which evolves hydrogen sulphide when acidified. When boiled for an hour with water or dilute alcohol, it is converted into the isomeric *thiocyanacetylethylurethane*, $COOEt\cdot NH\cdot CO\cdot CH_2\cdot SCN$; this melts at 174°, and dissolves in hot aqueous caustic soda with evolution of ammonia and formation of thioglycollic acid. *Thiocarbimido-* and *thio-cyan-acetylamylurethanes* are obtained by similar methods and exhibit similar reactions; they melt at 58° and 147° respectively.

When chloracetocarbamide is boiled with potassium thiocyanate in alcoholic solution, three products are obtained in addition to potassium chloride. One of these compounds, *thiocyanacetocarbamide*,

$$NH_2\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot SCN,$$
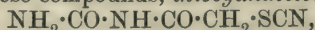
is insoluble in alcohol and decomposes without melting when heated. Of the two others, the less soluble in alcohol is thiohydantoin,

$$CS\begin{subarray}{l} \diagup NH\cdot CH_2 \\ \diagdown NH\cdot CO \end{subarray} \quad \text{or} \quad NH\!:\!C\begin{subarray}{l} \diagup NH\cdot CO \\ \diagdown S\!-\!CH_2 \end{subarray},$$ and the more soluble ethylic

allophanate, $NH_2\cdot CO\cdot NH\cdot COOEt$. Probably thiocarbimidoaceto-carbamide, $NH_2\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot NCS$, is the first product, but is converted to some extent into the isomeric thiocyanacetocarbamide, whilst to a still larger extent it decomposes into thiohydantoin and

cyanic acid, the latter of which at once reacts with ethylic alcohol to form ethylic allophanate. When chloracetocarbamide and potassium thiocyanate are heated together in aqueous solution, thiohydantoin is formed as before, and carbonic anhydride evolved, but apparently no thiocyanacetocarbamide is produced; no doubt the carbonic anhydride results from the action of water on the nascent cyanic acid.

When chloracetomethylcarbamide, $NHMe \cdot CO \cdot NH \cdot CO \cdot CH_2Cl$, is heated with potassium thiocyanate in alcoholic solution, a smell of methylcarbimide is observed, and thiohydantoin, together with crystalline *thiocyanacetomethylcarbamide*, $NHMe \cdot CO \cdot NH \cdot CO \cdot CH_2 \cdot SCN$, can be isolated from the product; in aqueous solution the same result is obtained (it is noteworthy that methylcarbimide and thiohydantoin are formed, not carbimide and methylthiohydantoin).

When *chloracetylphenylcarbamide*, $NHPh \cdot CO \cdot NH \cdot CO \cdot CH_2Cl$ (which is prepared from chloracetic chloride and phenylcarbamide and melts at 160°) is boiled with potassium thiocyanate in aqueous solution, carbonic anhydride is evolved and diphenylcarbamide, thiohydantoin, and pulverulent *thiocyanacetylphenylcarbamide*,

$$NHPh \cdot CO \cdot NH \cdot CO \cdot CH_2 \cdot SCN,$$
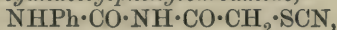
are also formed; doubtless the first two result from the decomposition of "nascent" phenylcarbimide. In alcoholic solution, thiocyanacetyl-phenylcarbamide, thiohydantoin and phenylurethane are formed, the last doubtless as a result of the action of the alcohol on nascent phenylcarbimide; some diphenylcarbamide is obtained in this case also, due probably to the presence of water in the alcohol.

C. F. B.

Molecular Rearrangement of Alkylic *Thioncarbamates. By HENRY L. WHEELER and BAYARD BARNES (*Amer. Chem. J.*, 1899, **22**, 141—151).—When methylic thioncarbamate, $NH_2 \cdot CS \cdot OMe$, is dissolved in methylic iodide (1 mol.), the solution becomes warm, and finally solidifies to a mass of crystals of methylic thiolcarbamate, $NH_2 \cdot CO \cdot SMe$; this crystallises from water and melts at 107—108°, not at 95—98°, as stated by Blankenhorn (Abstr., 1878, ii, 215), and is also formed by the action of methylic iodide on ethylic thioncarbamate. This is explained by assuming that in both reactions an intermediate additive compound is formed; in the case of ethylic thioncarbamate, $NH_2 \cdot CS \cdot OEt$, this would have either the structure $NH_2 \cdot C(OEt) \vdots SMeI$, assuming sulphur to be quadrivalent, or $NH_2 \cdot C(OEt)I \cdot SMe$, assuming it to be bivalent, and, by the loss of ethylic iodide, would give rise to methylic thiolcarbamate, $NH_2 \cdot CO \cdot SMe$.

When ethylic thioncarbamate is left in contact with ethylic iodide, it yields ethylic thiolcarbamate ("carbonylsulphethylamine," Conrad and Salomon, Abstr., 1875, 753), which melts at 107—108°.

Isoamylic thioncarbamate, in contact with isopropylic iodide, gives rise to *isopropylic thiolcarbamate*, $NH_2 \cdot CO \cdot SPr^\beta$, which crystallises from water in colourless, rectangular plates, and melts at about 125°.

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* The authors adopt the Geneva nomenclature, *thion* being used to denote compounds containing the group $\cdot CS \cdot OR$, and *thiol* those containing the group $\cdot CO \cdot SR$.

Isobutylic thioncarbamate, $NH_2 \cdot CS \cdot O \cdot C_4H_9$, prepared by the action of alcoholic ammonia on isoamylic ethyldithiocarbonate, $SEt \cdot CS \cdot O \cdot C_5H_{11}$, crystallises from ether or water in white plates and melts at 51—53°, not at 36° (Mylius, *Ber.*, 1872, **5**, 976), or 10° (Blankenhorn, *loc. cit.*): with dilute alcoholic silver nitrate, it produces a white precipitate which turns black; with mercuric chloride, a permanently white precipitate; with copper sulphate, a white precipitate which becomes black on warming, and with platinic chloride, a yellow precipitate which, when warmed, decomposes. *Isobutylic thiolcarbamate*, $NH_2 \cdot CO \cdot S \cdot C_4H_9$, prepared by heating it with isobutylic iodide at 120° for several hours, crystallises from water in thin, snow-white plates and melts at 102—103°; with both silver nitrate and mercuric chloride, it forms a white precipitate which does not blacken, but with copper sulphate and platinic chloride, no precipitate is produced.

Isoamylic thioncarbamate (Johnson, this Journal, 1853, **5**, 142), when heated with isoamylic iodide, yields the corresponding thiolcarbamate, $NH_2 \cdot CO \cdot S \cdot C_5H_{11}$, melting at 112—113°, not at 107° (Schöne, Abstr., 1886, 337).

When ethylenic bromide is heated with ethylic thioncarbamate for 3 hours at 100°, the *ethylene* derivative, $NH_2 \cdot CO \cdot S \cdot CH_2 \cdot CH_2 \cdot S \cdot CO \cdot NH_2$, of thiolcarbamic acid is obtained as a crystalline powder, together with small quantities of ethylic thiolcarbamate; the compound $NH_2 \cdot CO \cdot S \cdot CH_2 \cdot CH_2Br$ is not formed.

In the light of these results, the fact observed by Debus (*Annalen*, 1849, **72**, 18), that ethylic thioncarbamate, when heated, gives rise to ethyl mercaptan and cyanuric acid, is explained; it is probable that, in the first instance, the isomeric thiolcarbamate is formed by molecular rearrangement. The authors discuss the structure of the ammonium thiocarbamate, formed by the action of ammonia on carbon oxysulphide, and point out that the argument for Fleischer's formula, $NH_2 \cdot CO \cdot SNH_4$ (*Ber.*, 1876, **9**, 991), based on the fact that ethylic thiolcarbamate is formed when the compound is heated with ethylic bromide at 100°, does not preclude the thion structure; moreover, the ease with which the salt is desulphurated points to its being $NH_2 \cdot CS \cdot ONH_4$, for the analogous compound, $NH_2 \cdot CS \cdot OEt$, is readily desulphurated by silver nitrate, whilst the compound $NH_2 \cdot CO \cdot S \cdot C_7H_7$ yields a stable silver salt.   W. A. D.

Benzoylfurfuran. By R. MARQUIS (*Compt. rend.*, 1899, **129**, 111—113).—*Benzoylfurfuran*, $C_4OH_3 \cdot CO \cdot Ph$, obtained by the action of pyromucic chloride on benzene in the presence of aluminium chloride, is a colourless liquid which boils at 185° under 43 mm. pressure, does not solidify at −15°, and has a sp. gr. 1·183 at 19°. On oxidation with potassium permanganate, it gives benzoic acid and another acid melting at 52°, which has not yet been further studied. The *oxime* forms fine, yellow needles, is very soluble in organic solvents, melts at 132°, and is decomposed at a slightly higher temperature; with acetic anhydride, it gives two *acetyl* derivatives melting at 68° and 109° respectively. *Phenylfurfurylamine*, $C_4OH_3 \cdot CHPh \cdot NH_2$, prepared by reduction of an alcoholic solution of the oxime with metallic sodium, is a colourless liquid which has a faint odour, becomes brown

even in the dark, and loses ammonia spontaneously. It boils at 167—168° under 43—44 mm. pressure. The *acetyl* derivative melts at 127°. The *hydrochloride* forms extremely soluble, small prisms. The *platinochloride*, $(C_{11}H_{11}NO)_2,H_2PtCl_6 + 2H_2O$, crystallises in small, golden plates easily soluble in hot, but only slightly so in cold water; it decomposes at 100°. H. R. Le S.

Methylpentamethylene and its Derivatives. By WLADIMIR B. MARKOWNIKOFF (*Annalen*, 1899, **307**, 335—367. Compare Abstr., 1898, i, 637).—Methylpentamethylene (methylcyclopentane) is a limpid liquid having the odour of light petroleum; it boils at 71—72° under 759 mm. pressure, does not solidify at −79°, and has a sp. gr. 0·76406 at 0°/0° and 0·7430 at 20°/0° (compare Abstr., 1897, i, 401). Fuming nitric acid of sp. gr. 1·55 acts but slowly on the hydrocarbon if the mixture is kept cold, but above 0° action takes place with great violence; a mixture of nitric and sulphuric acids, however, is almost without action. Methylpentamethylene and its homologues are not alone in their activity towards nitric acid, which also attacks the substituted hexamethylenes.

1 : 3-*Methylketopentamethylene* (1 : 3-*Methylcyclopentanone*), the ketone obtained by distilling the calcium salt of β-methyladipic acid, yields the *oxime* in two modifications, which crystallise in needles, and melt at 67—69° and 87—89·5° respectively (compare Semmler, Abstr., 1893, i, 130).

3 : 1-*Amidomethylpentamethylene*, $\begin{matrix} \text{CHMe}\text{---}\text{CH}_2 \\ \text{CH}_2\cdot\text{CH(NH}_2) \end{matrix}{>}\text{CH}_2$, prepared by reducing the oxime in alcoholic solution with sodium, has a powerful ammoniacal odour, and mixes with water in all proportions; it boils at 124° under 754 mm. pressure, and has a sp. gr. 0·8594 at 0°/0°, 0·8422 at 20°/0°, and 0·8429 at 20°/20°. The *hydrochloride* dissolves readily in water and is optically inactive, whilst the *platinochloride* crystallises in orange leaflets; the *benzoyl* derivative separates from dilute alcohol in slender needles and melts at 115—117°.

3 : 1-*Hydroxymethylpentamethylene* (1 : 3-*Methylpentamethylenol*), $\begin{matrix} \text{CHMe}\text{---}\text{CH}_2 \\ \text{CH}_2\cdot\text{CH(OH)} \end{matrix}{>}\text{CH}_2,$ obtained on reducing the ketone in moist ether with sodium, boils at 150—151° (uncorr.). The secondary *iodide*, prepared by heating the alcohol with hydriodic acid, iodine, and red phosphorus at 100° during 8 hours, boils at 177—179° with slight decomposition.

1 : 1-*Nitromethylpentamethylene*, $\begin{matrix} \text{CMe(NO}_2)\cdot\text{CH}_2 \\ \text{CH}_2\text{---}\text{CH}_2 \end{matrix}{>}\text{CH}_2$, a colourless liquid having the odour of turpentine and camphor, boils at 92° under 40 mm. pressure without decomposition, but under 750 mm. pressure it decomposes, and the boiling point rises from 177° to 184°. Its sp. gr. is 1·0568 at 0°/0°, 1·0400 at 20°/0°, and 1·0453 at 15°/15°.

1 : 1-*Amidomethylpentamethylene*, $\begin{matrix} \text{CMe(NH}_2)\cdot\text{CH}_2 \\ \text{CH}_2\text{---}\text{CH}_2 \end{matrix}{>}\text{CH}_2$, obtained by reducing the nitro-compound with tin and hydrochloric acid, is an ammoniacal liquid which fumes in air and dissolves readily

in water; it boils at 114° under 753 mm., and has a sp. gr. 0·8367 at 0°/0°, and 0·8197 at 20°/0°. The *hydrochloride* melts above 240°, and the *hydrobromide* crystallises in long needles; the *platinochloride*, $(C_6H_{13}N)_2,H_2PtCl_6 + H_2O$, forms orange-red octahedra, darkens at 205°, and decomposes at 220°. The *aurichloride* crystallises in very long, orange-yellow needles, and decomposes at 172—174°; the *auribromide* forms black leaflets.

1 : 1-*Methylpentamethylenol*, $\begin{array}{c}CMe(OH)\cdot CH_2\\ | \quad\quad\quad\\ CH_2\text{———}CH_2\end{array}\!\!>\!CH_2$, formed from the amine by the action of nitrous acid, solidifies in long, transparent needles at 32°, and boils at 135—136°, when it decomposes in part. Fuming hydrochloric acid converts it into the *chloride*, which boils at 97° and 122—123° under pressures of 349 mm. and 757 mm. respectively, in part decomposing at the higher temperature, yielding a hydrocarbon, C_6H_{10}, and hydrogen chloride.

Methylcyclopentene-1 : 2, $\begin{array}{c}CMe\cdot CH_2\\ || \quad\quad\\ CH\text{——}CH_2\end{array}\!\!>\!CH_2$, a bye-product in the preparation of the alcohol, boils at 72° under 754 mm. pressure; when mixed with 6 parts of slightly fuming hydrochloric acid, the temperature rises to 28°, and after 15 minutes interval the hydrocarbon becomes green, and the acid, black.

The 2-*chloride*, $\begin{array}{c}CH_2Me\cdot CH_2\\ | \quad\quad\quad\\ CHCl\text{——}CH_2\end{array}\!\!>\!CH_2$, boils at 126°, and has a sp. gr. 0·9281 at 0°/0°, the *hydrocarbon*, C_6H_{10}, obtained from it by reduction, boils at 69—70° under 756 mm. pressure, and has a sp. gr. 0·7352 at 0°/0°.

2 : 1-*Nitromethylpentamethylene*, $\begin{array}{c}CHMe\text{——}CH_2\\ | \quad\quad\quad\\ CH(NO_2)\cdot CH_2\end{array}\!\!>\!CH_2$, boils at 185—186° under 758 mm. pressure, when it decomposes; its sp. gr. is 1·0462 at 0°/0° and 1·0296 at 20°/0°.

2 : 1-*Amidomethylpentamethylene*, $\begin{array}{c}CHMe\text{——}CH_2\\ | \quad\quad\quad\\ CH(NH_2)\cdot CH_2\end{array}\!\!>\!CH_2$, boils at 121—122° under 738 mm. pressure; its sp. gr. is 0·8179 at 0°/0° and 0·8006 at 20°/0°. The *hydrochloride* crystallises in small needles, and the *platinochloride*, $(C_6H_{13}N)_2,H_2PtCl_6$, begins to decompose at 240°; the *aurichloride* crystallises in lustrous, pale yellow leaflets, with $1H_2O$, and at 100° dissolves in its water of crystallisation.

M. O. F.

Structure of the so-called Hexanaphthenecarboxylic Acid. By WLADIMIR B. MARKOWNIKOFF (*Annalen*, 1899, 307, 367—374).— The existence of pentamethylene derivatives in Caucasian naphtha suggested the identity of Aschan's hexanaphthenecarboxylic acid with methylpentamethylenecarboxylic acid, $\begin{array}{c}CH_2\cdot CHMe\\ | \quad\quad\quad\\ CH_2\text{——}CH_2\end{array}\!\!>\!CH\cdot COOH$. This is now shown to be the case by converting the methylic salt into the amide, and the latter into the amine, which is found to be identical with 2 : 1-amidomethylpentamethylene, described in the foregoing abstract.

M. O. F.

Isomerisation in the Synthesis of Aromatic Hydrocarbons by Friedel's Reaction. III. Synthesis of Amylbenzene and its Derivatives. By MICHAEL KONOWALOFF and J. EGOROFF (*Chem. Centr.*, 1899, i, 776—777; from *J. Russ. Chem. Soc.*, 1898, **30**, 1031—1035. Compare *J. Russ. Chem. Soc.*, **26**, 202; **27**, 456).—By the action of isoamylic chloride on benzene in presence of aluminium chloride, amylbenzene is formed. This compound boils at 187—189° under 755 mm. pressure, and by the action of nitric acid at 105° yields secondary nitroamylbenzene and tertiary nitrophenylmethylisopropylmethane. The former compound is obtained in solution by distilling off the unchanged hydrocarbon and then treating with sodium ethoxide and afterwards with water, whilst the latter remains undissolved.

Secondary nitroamylbenzene, $NO_2 \cdot CHPh \cdot CH_2 \cdot CHMe_2$, boils at 159—161° under 20 mm. pressure, has a sp. gr. 1·08991 at 0°/0°, 1·07362 at 20°/0°, and a specific refractive index $[n]_D$ 1·53140 at 20°; it gives the pseudonitrol reaction with nitrous acid and is oxidised to benzoic acid by potassium permanganate. The *amine*, prepared by reducing the nitro-compound with tin and hydrochloric acid, boils at 232—235° under 756 mm. pressure, forms crystalline salts, and absorbs carbonic anhydride with avidity.

Tertiary nitrophenylmethylisopropylmethane, $NO_2 \cdot CMePh \cdot CHMe_2$, boils at 151—153° under 20 mm. pressure, has a sp. gr. 1·09414 at 0°/0°, 1·07825 at 20°/0°, and a specific refractive index $[n]_D$ 1·520402 at 20°. The *amine* boils at 226—227° under 739 mm. pressure, has a sp. gr. 0·95239 at 0°/0°, 0·93482 at 20°/0°, specific refractive index $[n]_D$ 1·51781 at 20°, and forms crystalline salts; when oxidised by potassium permanganate, the hydrochloride forms benzoic acid.

Besides isoamylbenzene and phenylmethylisopropylmethane, the product of the original reaction contains a hydrocarbon which is not attacked even by repeatedly treating with nitric acid. This compound is probably phenyldimethylethylmethane, $CMe_2Ph \cdot CH_2Me$; it boils at 189—191° and has sp. gr. 0·8889 at 0°/0° and 0·8740 at 20°/0°.

The following conclusions are deduced from these results. (1) Isoamylic chloride, when treated with benzene by Friedel's reaction, is not completely converted into isomerides either at a low temperature or at the boiling point of benzene. (2) Two types of isomerides are formed, the isoamyl radicle, $\cdot CH_2 \cdot CH \cdot CHMe_2$, becoming either $\cdot CHMe \cdot CHMe_2$ or $\cdot CEtMe_2$.   E. W. W.

Isomerisation in the Synthesis of Aromatic Hydrocarbons by Friedel's Reaction, IV. Isomerisation of the Isobutyl Radicle. By MICHAEL KONOWALOFF (*Chem. Centr.*, 1899, i, 777; from *J. Russ. Chem. Soc.*, 1898, **30**, 1036—1040. Compare preceding abstract).—The product of the action of isobutylic chloride on toluene in presence of aluminium chloride boils at 188—188·5° and when treated with nitric acid forms the *nitro*-derivatives, $NO_2 \cdot CH_2 \cdot C_6H_4 \cdot CMe_3$ [$CH_2:CMe_3 = 1:3$ and $1:4$], of the corresponding methyl-tertiary-butylbenzenes. The potassium salts obtained from this mixture, when oxidised by potassium permanganate, yield terephthalic, meta-butylbenzoic, and parabutylbenzoic acids, and give the nitrolic acid reaction. In this case, therefore, the isobutyl radicle, $CHMe_2 \cdot CH_2 \cdot$,

has been completely converted into the tertiary butyl radicle, ·CMe₃, the methyl group of the toluene having no influence on the extent of the isomerisation of the radicle united to the halogen. The formation of butylbenzoic acids is opposed to the rule that the longer side chain is oxidised to carboxyl; this oxidation of the longer chain, however, is really due, not to its length, but to its containing CH_2- or CH-groups attached directly to the benzene ring, such groups being more easily oxidised than methyl groups. In this case, however, the longer side chain has no such groups and the methyl is therefore attacked.   E. W. W.

Phenylic Chlorocarbonates. By ETIENNE BARRAL and ALBERT MOREL (*Bull. Soc. Chim.*, 1899, [iii], **21**, 727—728. Compare this vol., i, 747).—*Phenylic chlorocarbonate*, $COCl·OPh$, is a colourless liquid which rapidly becomes red; it boils without decomposition at 95° under 20 mm. and at 97—98° under 25 mm. pressure, but under the ordinary pressure it boils at 187°, decomposing into phosgene and diphenylic carbonate. *Orthotolylic chlorocarbonate*, $COCl·O·C_6H_4Me$, is a colourless liquid which rapidly becomes violet; it boils at 119° under 35 mm. at 114° under 25 mm. pressure, and when boiled under the ordinary pressure decomposes into phosgene and di-orthotolylic carbonate. *Guaiacylic chlorocarbonate*, $COCl·O·C_6H_4·OMe$, boils at 112° under 25 mm. pressure, but decomposes when boiled under the ordinary pressure, yielding diguaiacylic carbonate. *Thymylic chlorocarbonate*, $COCl·O·C_6H_3MePr$, boils at 122—124° under 25 mm. pressure, and when boiled under ordinary conditions yields dithymylic carbonate.   W. A. D.

[**Derivatives of Ethoxyphenol.**] By EMANUEL MERCK (*Chem. Centr.*, 1899, i, 706; from *Jahresber.*, 1898, 25—142).—*Ethoxyphenylic benzoate*, $OEt·C_6H_4·OBz$ [OEt : OBz = 1 : 2] forms colourless crystals, melts at 31°, and is easily soluble in alcohol or ether; the *salicylate*, $OEt·C_6H_4·O·CO·C_6H_4·OH$, forms colourless crystals, melts at 40—41°, and is soluble in alcohol or ether; the *butyrate*, $OEt·C_6H_4·O·COPr$, is a colourless liquid, boils at 260°, and is miscible with alcohol or ether; the *valerate*, $OEt·C_6H_4·O·CO·C_4H_9$, is a colourless liquid, boils at 262°, and is miscible with alcohol, ether, or chloroform; the *phosphate*, $(OEt·C_6H_4·O)_3PO$, forms colourless crystals, melts at 131—132°, and is soluble in alcohol.   E. W. W.

Egols. New Antiseptics. By E. GAUTRELET (*Compt. rend.*, 1899, **129**, 113—114).—Orthonitro-phenol-, cresol-, or thymol-parasulphonic acid easily absorbs half an atomic proportion of mercury. To the resulting parasulphonates of mercury and potassium, the generic name of *egol* is given, each compound being distinguished by a prefix indicating the phenol from which it is derived, thus: *phenegol, cresegol, thymegol*. The egols are very stable compounds, from which mercury can be separated only by heating with soda-lime or by treating with potassium chlorate and hydrochloric acid. They form red-brown powders, are difficult to crystallise, and dissolve in water, but not in strong alcohol. The aqueous solutions are odourless, neutral, and

non-irritant, do not coagulate albumins, are not decomposed by organic substances, and precipitate the toxins. They are not toxic, as, when introduced hypodermically, 2 grams per kilo. of the weight of the animal are required to cause death, but are powerful bactericides, 4 grams per 1000 introduced into a culture preventing all bacterial growth. H. R. LE S.

Condensation of Succinic Anhydride and Pyrogallol. By GEORG VON GEORGIEVICS (*Monatsh.*, 1899, 20, 450—461).—The author has isolated two dyes from the numerous substances which are formed by the condensation of succinic anhydride and pyrogallol.

Pyrogallolsuccinein, $C_{16}H_{14}O_8$, is obtained when a mixture of equal parts of succinic anhydride and zinc chloride is heated for several hours at 170° with an equal weight of pyrogallol. It forms a reddish-brown powder, is practically insoluble in the ordinary solvents, and decomposes at 180°. When boiled with alcoholic hydrochloric acid, it yields a *monohydrochloride* crystallising in brownish-yellow, microscopic plates. The *sulphate* crystallises from concentrated sulphuric acid in dark-blue crystals. The colouring properties of pyrogallolsuccinein are very similar to those of gallein.

Digallacyl, $C_6H_2(OH)_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot C_6H_2(OH)_3$, is prepared by heating a fused mixture of 1 part of succinic anhydride and 2 parts of pyrogallol for 10 minutes at 150° with one-third its weight of zinc chloride. It crystallises in tufts of slender, glistening, colourless needles, and darkens, without fusing, at about 270°. It dissolves in alcohol or acetic acid, but is almost insoluble in other ordinary solvents; strong caustic soda dissolves it, forming a yellow solution, whilst in cold concentrated sulphuric acid it forms a yellow solution which, when warmed, suddenly becomes a deep violet. As a dye, it is very similar to gallacetophenone. *Hexacetyldigallacyl* forms microscopic prisms, melts at 170—171°, and is very soluble in acetic acid, but almost insoluble in alcohol. *Digallacylosazone* crystallises from alcohol with 1 mol. of the solvent in tufts of yellowish needles, darkens in colour about 190°, and decomposes suddenly at 206—207°. R. H. P.

Isomeric Change in [the Formation of] Homologues of Phloroglucinol. By R. REISCH (*Monatsh.*, 1899, 20, 488—503).— Various homologues of phloroglucinol, in methyl alcoholic solution, were treated successively with sodium methoxide and methylic iodide. Trimethylphloroglucinol gave a quantitative yield of hexamethyl-phloroglucinol : dimethylphloroglucinol a mixture of hexamethyl- and tetramethyl-phloroglucinol : monomethylphloroglucinol, a mixture of hexamethyl-, pentamethyl-, and tetramethyl-phloroglucinol : products exclusively of the ketonic type. Trimethylphloroglucinol monomethylic ether yielded pentamethylphloroglucinol monomethylic ether ; dimethyl-phloroglucinol gave a product soluble in alkali, probably tetramethyl-phloroglucinol, together with tetra- and probably penta-methylphloro-glucinol monomethylic ether ; monomethylphloroglucinol monomethylic ether gave a mixture of tetra- and penta-methylphloroglucinol mono-methylic ethers : no increase in the number of methoxyl groups occurs, ketonic compounds being formed as the result of methylation.

Tetramethylphloroglucinol monomethylic ether, $C_6HMe_4O_2 \cdot OMe$, crystallises in colourless, glistening plates [$a : b : c = 0.7039$; $\xi = 92° 1'$: $\eta = 79° 6'$; $\zeta = 98° 6'$], melts at 63°, boils at 143° under 16 mm. pressure, dissolves very readily in alcohol, benzene, or ethylic acetate, but less readily in light petroleum, and is insoluble in water. The *pentamethyl* derivative is a yellowish, thick liquid and boils at 139° under 19 mm. pressure. R. H. P.

Filicic Acid. By RUDOLF BOEHM (*Annalen*, 1899, **307**, 249—282. Compare Abstr., 1898, i, 40, and this vol., i, 32).—The author represents the constitution of filicic acid by one of the formulæ $CMe_2\!\!<\!\!{}^{C(OH)\colon CH}_{C(OH)\colon CH}\!\!>\!\!CO$, and $CMe_2\!\!<\!\!{}^{C(OH)\colon CH}_{CO\text{——}CH}\!\!>\!\!C\cdot OH$, which illustrate the close relation between this compound and phloroglucinol ; tetrabromofilicic acid has the constitution expressed by the formula $CMe_2\!\!<\!\!{}^{CO\cdot CBr_2}_{CO\cdot CBr_2}\!\!>\!\!CO$.

Filicic acid crystallises from alcohol in small, colourless cubes, and melts at 213—215°, when it becomes brown ; the aqueous solution develops a red coloration with ferric chloride, and reduces potassium permanganate and an ammoniacal silver solution. On adding a colourless specimen of aniline to the alcoholic solution, a beautiful, reddish-violet coloration is slowly developed ; when the crystalline acid is heated with aniline and acetic anhydride or glacial acetic acid, an emerald green coloration is gradually produced. The *methyl ether*, $C_8H_9O_2 \cdot OMe$, prepared by saturating a hot solution of filicic acid in methylic alcohol with hydrogen chloride, crystallises from ethylic acetate in colourless, lustrous prisms, and melts at 208° ; it dissolves with difficulty in boiling water, and develops a violet red coloration with ferric chloride. The *ethyl ether* crystallises from alcohol in lustrous prisms, and melts at 215° ; the *diethyl ether*, $C_8H_8O(OEt)_2$, prepared by heating it with ethylic iodide and alcoholic potash, crystallises from light petroleum in quadratic plates or long prisms melting at 103—105°, and is indifferent towards ferric chloride. The *diacetyl* derivative, $C_8H_8O(OAc)_2$, crystallises from alcohol in large, six-sided plates and melts at 82—85° ; it is indifferent towards ferric chloride. When the potassium salt of filicic acid is oxidised with potassium permanganate, 35 per cent. of dimethylmalonic acid is produced.

The *dichloride* of filicic acid, $C_8H_8Cl_2O$, prepared by the action of phosphorus pentachloride, crystallises from light petroleum in six-sided and rhombic plates, melting at 79—80°. The *compound*, $C_8H_9O_2 \cdot O \cdot POCl_2$, arising from the action of phosphorus oxychloride, occurs as a bye-product ; it crystallises from chloroform in small plates, and decomposes at 158—160°.

Dibromofilicic acid, $C_8H_8Br_2O_3$, prepared by suspending filicic acid in absolute alcohol and slowly adding bromine, crystallises from carbon bisulphide in large, colourless prisms, and melts at 147—148° ; exposure to air causes the substance to become yellow, and change gradually into bromofilicic acid, which is also produced when the

dibromo-compound is digested with glacial acetic acid or with boiling water.

Tribromofilicic acid, $C_8H_7Br_3O_3$, obtained when bromine acts on filicic acid in the dry state or suspended in glacial acetic acid, crystallises from carbon bisulphide in lustrous, rhombic plates and prisms, becoming yellow at 120° and melting at 132°.

Bromofilicic acid, $C_8H_9BrO_3$ or $C_8H_7BrO_3$, produced when either of the foregoing bromo-compounds is digested with boiling water, dissolves with difficulty in common solvents excepting acetone; it crystallises from glacial acetic acid in small, orange-red cubes and quadratic plates, and decomposes without fusion above 250°. Filicic acid is regenerated when the bromo-derivative is reduced with sodium amalgam, and oxidation with potassium permanganate gives rise to dimethylmalonic acid.

Tetrabromofilicic acid (*dimethyltetrabromocyclohexane*-1 : 3 : 5-*trione*), $C_8H_6Br_4O_3$, formed when tribromofilicic acid is dissolved in excess of bromine, is best prepared by slowly adding bromine to a neutral or feebly alkaline solution of filicic acid in aqueous potash; it crystallises from alcohol in lustrous prisms and six-sided plates, melting at 139°. The alcoholic solution is indifferent towards ferric chloride, but liberates iodine from potassium iodide. Caustic alkalis act readily on tetrabromofilicic acid, converting it into hexabromodimethylacetyl-acetone, and the *compound*, $C_7H_7BrO_3$, which crystallises from water in colourless, lustrous prisms containing $1\frac{1}{2}H_2O$, melts at 179—180° when anhydrous, develops an intense red coloration with ferric chloride and yields a crystalline *barium* salt.

Hexabromodimethylacetylacetone, $CMe_2(CO \cdot CBr_3)_2$, is prepared by adding finely powdered filicic acid to a large excess of bromine, and, after an interval, adding 15 per cent. caustic soda until the liquid is alkaline; it separates from glacial acetic acid in large, lustrous crystals, and melts at 149—150°. The alcoholic solution is indifferent towards ferric chloride, and liberates iodine from potassium iodide.

Tetrabromodimethylacetylacetone, $C_7H_8Br_4O_2$, obtained by adding bromine to dimethylacetylacetone until action ceases and allowing the excess of halogen to evaporate, crystallises from light petroleum in large, lustrous prisms and melts at 78°; further treatment with bromine leaves the substance unchanged, but if a solution in the halogen is treated with 15 per cent. caustic soda, hexabromodimethyl-acetylacetone is produced.

Tetrachlorofilicic acid, $C_8H_6Cl_4O_3$, prepared by saturating with chlorine a solution of filicic acid in chloroform, crystallises in snow-white prisms several centimetres in length; it melts at 83—84°.

Symmetrical tetrachlorodimethylacetylacetone, $CMe_2(CO \cdot CHCl_2)_2$, formed from tetrachlorofilicic acid by the action of water, crystallises from light petroleum in large, lustrous prisms, and melts at 95—96°.

M. O. F.

Optical Activity of Tannin. By FLAVIAN FLAWITZKY (*Chem. Centr.*, 1899, i, 327; from *J. Russ. Chem. Soc.*, 1898, **30**, 748—749). —A remark of Walden (*Ber.*, 1897, **30**, 3151) makes the author call attention to the fact that he was the first to determine the optical

activity of tannin (*J. Russ. Chem. Soc.*, **22**, 362). The specific rotation of tannin for sodium and lithium light is as follows : $[a]_\gamma +50\cdot3°$ for $c=13\cdot11$ in water, $[a]_D$ 58° for same solution decolorised by animal charcoal ; $[a]_D$ 22° and $[a]_\gamma$ 17·4° for $c=4\cdot596$ in ethylic alcohol ; $[a]_D$ 24·5° and $[a]_\gamma$ 19·4° for $c=11\cdot576$ in acetic acid.   J. C. P.

Action of Paranitrobenzylic Chloride on Dimethylaniline and on Diphenylamine. By EDGAR WEDEKIND [and J. GONSWA] (*Annalen*, 1899, **307**, 283—293).—*Phenylparanitrobenzyldimethylammonium chloride*, $C_{15}H_{17}N_2O_2Cl$, produced when a mixture of dimethylaniline and paranitrobenzylic chloride is left at the ordinary temperature for some months, crystallises from alcohol in four-sided plates belonging to the monoclinic system $[a:b:c=1\cdot3317:1:?$ $\beta=51°\ 17']$; it melts at 118—120°, and yields salts with gold and platinic chlorides.

If the foregoing mixture is heated until ebullition begins, vigorous action takes place, and methyl-violet is formed, along with *paranitrotetramethyldiamidotriphenylcarbinol*, $C_{23}H_{25}N_3O_3$, a pale yellow, crystalline substance, which sinters at 80°, and melts indefinitely at 100—105°; the *picrate* is a deep green powder melting to a brownish mass below 100°.

When paranitrobenzylic chloride is heated with diphenylamine until action takes place, diphenylamine-blue is obtained ; the nature of the bye-product has not been yet determined.   M. O. F.

Action of Aromatic Amines on Chloracetylurethanes and Chloracetocarbamides. By G. FRERICHS and HEINRICH BECKURTS (*Arch. Pharm.*, 1899, **237**, 331—346).—When a chloracetocarbamide, $NHR^1\cdot CO\cdot NH\cdot CO\cdot CH_2Cl$ (1 mol.), is heated on the water-bath with an amine, $NHR^{11}\cdot C_6H_4R^{111}$ (rather more than 2 mols.), the product is a glycocinylcarbamide, $NHR^1\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot NR^{11}\cdot C_6H_4R^{111}$ [R^1, R^{11}, R^{111} may each be H]. The following were obtained ; the numbers given are their melting points, and R^1, R^{11}, and R^{111} are to be understood as H where the contrary is not indicated. *Phenyl-glycocinylcarbamide*, 176° ; *2-tolyl-* [$R^{111}=$Me], 196° ; *4-tolyl*, 178° ; *4-ethoxyphenyl-* [$R^{111}=$OEt], 177° ; *methylphenyl-* [$R^{11}=$Me], 200° ; *ethylphenyl-* [$R^{11}=$Et], 200°. *Phenyl-glycocinyl-methyl-carbamide* [$R^1=$Me], 145° ; *4-ethoxyphenyl—methyl-* [$R^{111}=$OEt, $R^1=$Me], 170° ; *phenyl—phenyl-* [$R^1=$Ph], 160° ; *2-tolyl—phenyl-* [$R^{111}=$Me, $R^1=$Ph], 175° ; *4-tolyl—phenyl-*, 176° ; *4-ethoxyphenyl—phenyl-* [$R^{111}=$OEt, $R^1=$Ph], 154° ; *phenyl-4-ethoxyphenyl-* [$R^1=C_6H_4\cdot$OEt], 162° ; *2-tolyl-4-ethoxyphenyl-* [$R^{111}=$Me, $R^1=C_6H_4\cdot$OEt], 183° ; *4-tolyl-4-ethoxyphenyl-*, 172° ; *4-ethoxyphenyl-4-ethoxylphenyl-* [$R^{111}=C_6H_4\cdot$OEt, $R^1=$OEt], 162°. Such of these glycocinylcarbamides as have $R^{11}=$H lose ammonia or a substituted amine when heated to a high temperature, and yield β-hydantoins, $CO{<}^{N(C_6H_4R^{111})\cdot CH_2}_{NH\text{————}CO}$ (see below). These are also the direct products when the chloracetocarbamide is heated with the amine to a high temperature.

When a chloracetylurethane, $COOR\cdot NH\cdot CO\cdot CH_2Cl$, is heated at not too high a temperature, and for not too long a time, with an

amine, $NHR^{11} \cdot C_6H_4R^{111}$, preferably with the addition of a little alcohol, a glycocinylurethane, $COOR \cdot NH \cdot CO \cdot CH_2 \cdot NR^{11} \cdot C_6H_4R^{111}$, is formed. *Phenyl-glycocinyl-ethyl-urethane* [R = Et], 80°; 2-*tolyl–ethyl-* [R^{111} = Me, R = Et], 120°; 4-*tolyl–ethyl-*, 90—100°; 4-*ethoxyphenyl–ethyl* [R^{111} = OEt, R = Et], 100°; *methylphenyl–ethyl-* [R^{11} = Me, R = Et], 117°; *Methylphenyl–isobutyl-* [R^{11} = Me, R = iso-Bu], 103°. Such of these compounds as have R^{11} = H have a certain basic character, being very soluble in dilute acids; they also decompose when they melt. Moreover, they readily lose alcohol when heated alone or with caustic soda, forming β-hydantoins (see above); and in fact these are the products obtained directly when the chloracetylurethane is heated with the amine for some time on the water-bath. *β-4-Ethoxyphenyl-hydantoin* [R^{111} = OEt], melting at 234°, appears to be a new compound. These hydantoins are also formed when the substituted chloracetyl-phenylcarbamides are heated with alcoholic potash. With alkalis, they yield salts of the corresponding hydantoic acids; *potassium 4-ethoxyphenylhydantoate*, $NH_2 \cdot CO \cdot N(C_6H_4 \cdot OEt) \cdot CH_2 \cdot COOK$, was analysed. C. F. B.

Combination of Phenylhydrazine with Sodium Hydrogen Sulphite. By PASTUREAU (*J. Pharm.*, 1899, [vi], 9, 574—575. Compare this vol., i, 205). The precipitate formed when phenylhydrazine is added to a sodium hydrogen sulphite solution appears to have the composition $NaHSO_3, 2N_2H_3Ph$. It is very soluble in water, crystallises in colourless needles radiating from a centre, and decomposes when heated to 100°. H. R. Le S.

Compounds of Phenylhydrazine with Cuprous Salts. By JOSEPH MOITESSIER (*Bull. Soc. Chim.*, 1899, [iii], 21, 666—668).—The compounds which phenylhydrazine forms with cuprous chloride, bromide, and iodide are nearly insoluble in cold water, dissolve in sodium thiosulphate solution, and are decomposed by alcohol and ether, which dissolve out the phenylhydrazine. They gradually alter on exposure to air, especially when moist, and are rapidly decomposed at higher temperatures. *Phenylhydrazine cuprochloride*, $2Cu_2Cl_2, 5N_2H_3Ph$, obtained by adding excess of phenylhydrazine to a cold solution of cuprous chloride in 10 per cent. aqueous sodium chloride, crystallises in white needles; it begins to decompose at 65°, then becomes brown, and is rapidly decomposed at 110°.

Phenylhydrazine cuprobromide, $2Cu_2Br_2, 7N_2H_3Ph$, prepared by adding phenylhydrazine to cuprous bromide dissolved in aqueous potassium bromide, crystallises in slender, white needles which begin to decompose at 70° and undergo rapid decomposition at 110°.

Phenylhydrazine cupro-iodide, $Cu_2I_2, 4N_2H_3Ph$, obtained by adding phenylhydrazine (4 mols.) to cuprous bromide (1 mol.) dissolved in 20 per cent. sodium thiosulphate solution, crystallises in rhomboidal prisms, and is somewhat more stable than the preceding salts. When heated, decomposition commences at 100°, and becomes very rapid at 170°.

When phenylhydrazine is added to solutions of cupric haloids, reduction occurs, and the corresponding cuprous compounds are

obtained. Cupric sulphate and nitrate, under the same conditions, yield pale rose-coloured, crystalline precipitates, too unstable to permit of isolation, which are probably compounds of phenylhydrazine with cuprous sulphate and nitrate respectively. Similar reactions are found to occur when precipitated copper is added to a mixture of cupric salts with pyridine.   N. L.

Action of Phenylhydrazine on Alkylic Bromides, Chlorides, and Iodides. By JULES ALLAIN LE CANU (*Compt. rend.*, **129**, 105—106. Compare Genvresse and Bourcet, this vol., i, p. 501).—To a well-cooled ethereal solution of phenylhydrazine (1 mol.) was added gradually and with constant stirring half a mol. of ethylic bromide free from hydrogen bromide; at the end of 24 hours, there was a deposit in slender needles of a *compound*, which, on analysis, proved to be a combination of two mols. of phenylhydrazine with one of hydrogen bromide; it melts and decomposes at 195°, and on prolonged heating at 100° loses one mol. of phenylhydrazine; it is slightly soluble in ether, soluble in alcohol, and very soluble in water; its aqueous solution is acid, and with silver nitrate gives a white precipitate which blackens rapidly. If alcohol is employed as solvent in place of ether, phenylhydrazine hydrobromide is the product.

The action of ethylic chloride on phenylhydrazine is similar to that of ethylic bromide, the analogous compounds being formed both in ethereal and alcoholic solutions; the hydrochloride containing 2 mols. of phenylhydrazine melts at about 225° and is less stable than the corresponding hydrobromide.

The compounds $(PhN_2H_3)_2,C_3H_7I$ and $(PhN_2H_3)_2,C_4H_9I$ are formed by the action of propylic iodide and normal butylic iodide respectively on phenylhydrazine; the former crystallises from alcohol in brilliant needles, is soluble in water, but only slightly so in ether, and melts at 122°; the latter has similar properties, and melts at 126°.

                                                H. R. LE S.

Action of Phenylhydrazine on Chloracetocarbamides and Chloracetylurethane. By G. FRERICHS and HEINRICH BECKURTS (*Arch. Pharm.*, 1899, **237**, 346—358).—The chloracetocarbamide, $NHR^1 \cdot CO \cdot NH \cdot CO \cdot CH_2Cl$ [R = H,Me,Ph,$C_6H_4 \cdot OEt$] (1 mol.), was boiled for several hours with phenylhydrazine (2 mols.) in alcoholic solution; the alcoholic mother liquor contained yellow, resinous substances which have not yet been examined, whilst the solid which separated was in part soluble, in part insoluble, in very dilute hydrochloric acid. In the case of chloracetylurethane, $COOEt \cdot NH \cdot CO \cdot CH_2Cl$, no product soluble in hydrochloric acid was obtained.

The substances soluble in dilute hydrochloric acid were unsymmetrical phenylhydrazidacetocarbamides, $\mathrm{{}_1 NHR^1 \cdot CO \cdot NH \cdot CO \cdot CH_2 \cdot NPh \cdot NH_2}$. *Phenylhydrazidaceto-carbamide,* *-methylcarbamide,* *-phenylcarbamide,* and *-4-ethoxyphenylcarbamide* melt at 188°, 185°, 180°, and 169°, and their *benzylidene* derivatives at 219°, 238°, 177°, and 179° respectively. The first of these yields unsymmetrical phenylhydrazidacetic acid (Harries, Abstr., 1895, i, 460), with evolution of ammonia, when it is boiled with aqueous caustic soda.

The substances insoluble in dilute hydrochloric acid, in the case of the phenylic and 4-ethoxyphenylic compounds, were oxidation products, $NHR^1 \cdot CO \cdot NH \cdot CO \cdot CH \colon N \cdot NHPh$, of the symmetrical phenylhydrazido-derivatives, which doubtless were first formed; *phenylhydrazine-glyoxylyl-phenylcarbamide* and *-4-ethoxyphenylcarbamide* melt at 197° and 151° respectively. In the case of the methylic compound, the product was unfortunately lost. From chloracetocarbamide and -urethane, an identical product was obtained: probably a symmetrical phenylhydrazine, was formed as before, and then the central CO-group condensed with a second mol. of phenylhydrazine, when from the resulting compound, by elimination of ammonia in the one case and alcohol in the other, a *compound*, $\genfrac{}{}{0pt}{}{NPh-N}{CO \cdot NH}{>}C \cdot CH \colon N \cdot NHPh$,

was formed. This is yellowish, melts at 275°, and has a feebly acid character; a mono-*silver* derivative was prepared.

In the case of carbamide itself and of methylcarbamide the unsymmetrical derivatives form the main product; in the case of phenylcarbamide and 4-ethoxyphenylcarbamide about equal amounts of both derivatives are formed. This is in harmony with the fact, already recognised, that chloracetyl derivatives of radicles having an acid nature yield symmetrical derivatives of phenylhydrazine, whilst those of radicles having a basic nature yield unsymmetrical derivatives.

It has been shown in a previous paper (p. 806) that aromatic glycocinyl derivatives of carbamide readily yield β-hydantoins by elimination of ammonia. In a similar fashion, when unsymmetrical phenylhydrazidaceto-carbamide or -methylcarbamide is heated at about 200°, ammonia or methylamine is evolved and 1-*phenyldiketotetra-hydro-a-triazine*, $CO \genfrac{<}{>}{0pt}{}{NH \cdot NPh}{NH-CO} CH_2$, is formed; this melts at 229°

and has an acid character. C. F. B.

Acetylleucomethylene-Blue. By GEORG COHN (*Arch. Pharm.*, 1899, **237**, 385—390).—Acetylleucomethylene-blue,

$$NAc \genfrac{<}{>}{0pt}{}{C_6H_3(NMe_2)}{C_6H_3(NMe_2)} S$$
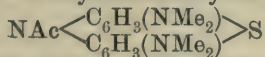
(Bernthsen, Abstr., 1883, 917), was prepared by mixing methylene-blue hydrochloride (1 part) with glacial acetic acid (1 part) and acetic anhydride (3 parts), adding zinc powder gradually, and heating gently until all coloration had disappeared, then adding fused sodium acetate, boiling for 1—2 hours in a reflux apparatus, and finally pouring the product into water. It is colourless; it melts at 179—181°, its *mercuri-chloride* melts at 127°, and its yellow *picrate* melts and decomposes at 184—185°; it is basic in character; various reagents convert it with moderate ease into a blue colouring matter, presumably methylene-blue; it is but little poisonous, and becomes oxidised to the blue colouring matter in the system.

Acetylleucoethylene-blue, $NAc \genfrac{<}{>}{0pt}{}{C_6H_3(NEt_2)}{C_6H_3(NEt_2)} S$, was prepared in the same way as the analogous methylene compound, and has similar properties; it melts at 179—180°. C. F. B.

Symmetrical Dinitroditolylcarbamides. By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], **21**, 659—665).—These compounds have been prepared by methods analogous to those employed in the preparation of the dinitrodiphenylcarbamides (this vol., i, 692), namely, by heating the various isomeric nitrotoluidines (2 mols.) with carbonyl chloride or with phenylic carbonate.

Dinitroditolylcarbamide, $CO(NH \cdot C_6H_3Me \cdot NO_2)_2$ [NH : Me : NO$_2$ = 2 : 1 : 5], from 5-nitrorthotoluidine, crystallises from boiling anhydrous acetic acid in small, white needles melting and subliming at 305—310°, and is insoluble in water, ether, benzene, or chloroform, slightly soluble in alcohol, more so in acetic acid. It is reduced by tin and hydrochloric acid to *diamidoditolylcarbamide*, $CO(NH \cdot C_6H_3Me \cdot NH_2)_2$, which crystallises from boiling 95 per cent. alcohol in small, white needles melting at 264—265°.

Dinitroditolylcarbamide, [NH : Me : NO$_2$ = 4 : 1 : 3], from 3-nitroparatoluidine, crystallises from boiling acetic acid in yellow needles melting and subliming at 244—245°, and is soluble in alcohol or benzene, but insoluble in water. It is not reduced by stannous chloride, but when heated with zinc dust and acetic acid is converted into *diamidoditolylcarbamide*, which crystallises in slender, white needles and is insoluble in water or benzene, but slightly soluble in boiling alcohol ; when heated, it sublimes without melting.

Dinitroditolylcarbamide, [NH : Me : NO$_2$ = 2 : 1 : 4], from 4-nitrorthotoluidine, crystallises from boiling acetic acid in small, white needles melting and subliming at 300—305°, and is insoluble in water, benzene, chloroform, or ether, slightly soluble in alcohol, more so in boiling acetic acid. On reduction with tin and hydrochloric acid, it yields *diamidoditolylcarbamide*, which crystallises in white, microscopic needles, decomposes when heated, and is insoluble in water, benzene, or ether, but dissolves very slightly in boiling alcohol.

Dinitroditolylcarbamide, [NH : Me : NO$_2$ = 4 : 1 : 2], from 2-nitroparatoluidine, is fairly soluble in boiling alcohol, acetic acid, or ethylic acetate, and crystallises either in white needles or in yellow prisms, in this respect resembling dimetanitrodiphenylcarbamide (*loc. cit.*). The two modifications melt at the same temperature, 251—252°, and when treated with tin and hydrochloric acid yield products having the characteristics of tolylenediamines mixed with a small quantity of *monamidoditolylcarbamide*, $C_6H_4Me \cdot NH \cdot CO \cdot NH \cdot C_6H_3Me \cdot NH_2$; when zinc dust and acetic acid are used, tolylenediamines alone are obtained.

3-Nitroparatoluidine, in which the NO$_2$ and NH$_2$ groups occupy the ortho-position with regard to each other, resembles orthonitraniline in entering into reaction with carbonyl chloride, but not with phenylic carbonate. N. L.

Action of Sulphuryl Chloride on Ethylic Metahydroxybenzoate. By GIROLAMO MAZZARA (*Gazzetta*, 1899, **29**, i, 371—383).— Whilst with ethylic salicylate, sulphuryl chloride gives rise to only one chloro-derivative (this vol., i, 700), in the case of ethylic metahydroxybenzoate two ethylic chlorohydroxybenzoates are obtained.

The acid corresponding with the ethylic salt comprising the liquid portion of the product is identical with the compound obtained by Peratoner and Condorelli (Abstr., 1898, i, 642), and has the constitution [COOH : OH : Cl = 1 : 3 : 6] ; it melts at 178°, the temperature given by Peratoner being 169—170°. *Methylic 6-chloro-3-hydroxybenzoate* separates from dilute alcohol in large, flat, glistening crystals melting at 100°. *Methylic 6-chloro-3-methoxybenzoate*, $OMe \cdot C_6H_3Cl \cdot COOMe$, is obtained as an oil, which on hydrolysis gives the methoxy-acid melting at 168—169°; Peratoner and Condorelli (*loc. cit.*) give the melting point 160—161°.

The solid portion of the chlorinated product consists of a hydrated *ethylic chlorohydroxybenzoate*, $OH \cdot C_6H_3Cl \cdot COOEt + H_2O$ [COOEt : OH : Cl = 1 : 3 : ?], crystallising from dilute alcohol in small, white needles, which, when heated, lose water and melt at 58° to a turbid liquid becoming transparent at a higher temperature ; it is readily soluble in cold ether or alcohol, and when treated with benzene at the ordinary temperature or heated with light petroleum loses water, the anhydrous compound remaining in solution. The *acid*, $OH \cdot C_6H_3Cl \cdot COOH$, melts at 156—157° and separates from benzene in prismatic plates, and from water in crystalline flocks ; in aqueous solution, it gives a reddish-violet coloration with ferric salts. Its *silver* salt is a white, crystalline precipitate becoming violet on exposure to light. The *methylic* salt, $OH \cdot C_6H_3Cl \cdot COOMe + H_2O$, crystallises from very dilute alcohol in long, white prisms melting at 70—71° with loss of water ; the anhydrous methylic salt melts at 62—65°. *Methylic chloromethoxybenzoate*, [COOMe : OMe : Cl = 1 : 3 : ?], separates from dilute alcohol in glistening needles melting at 41—42°. T. H. P.

Action of Sulphuryl Chloride on Alkylic Parahydroxybenzoates. By GIROLAMO MAZZARA [and A. ROLAND] (*Gazzetta*, 1899, 29, i, 383—389).—*Methylic 3-chloro-4-hydroxybenzoate*, $OH \cdot C_6H_3Cl \cdot COOH$, obtained by the interaction of sulphuryl chloride and ethylic parahydroxybenzoate in molecular proportions, separates from dilute alcohol in glistening, white, acicular crystals melting at 107°. The *methoxy-*derivative, $OMe \cdot C_6H_3Cl \cdot COOMe$, is deposited from dilute alcohol in sparkling, white crystals melting at 93—94°.

Ethylic 3-chloro-4-hydroxybenzoate, prepared by the interaction of sulphuryl chloride and ethylic parahydroxybenzoate, in molecular proportion, crystallises from alcohol in sparkling, flocky needles melting at 77—78°.

Ethylic 3 : 5-dichloro-4-hydroxybenzoate, obtained by the action of two mols. of sulphuryl chloride on one of ethylic parahydroxybenzoate, separates from dilute alcohol in small, white, acicular crystals melting at 116°, and is soluble in benzene or light petroleum. The acid melts at 257—258·5° ; Lössner gives 255—256° and Zincke 259—260°.

By the action of two mols. of sulphuryl chloride on one of methylic parahydroxybenzoate, methylic 3 : 5-dichloro-4-hydroxybenzoate melting at 121° is obtained.

A table is given of all the products obtained by the action of sulphuryl chloride on alkylic hydroxybenzoates. T. H. P.

Influence of Carbonyl on Adjacent Groups. By Daniel Vorlän-
der (*Chem. Centr.*, 1899, i, 729 ; from *Abhand. Naturforsch. Ges. Halle*,
21, 233—250).—The proximity of the carbonyl group renders the
hydrogen atoms attached to α-carbon atoms more easily replaceable, and
two carbonyl or negative groups (·CO·CH$_2$·CO· or ·CO·CH$_2$·CN) may
even cause the hydrogen atoms to be capable of ionisation (compare
von Schilling and Vorländer, *Annalen*, 1899, **308**, 184).   The prox-
imity of a carbonyl group to a double linking(·CH:CH·CO·), confers the
additive properties of ethylic sodiomalonate, &c., on αβ-unsaturated
alkylic salts and ketones.   Phenylethylene and the following
derivatives, C$_8$H$_7$Ph, C$_8$H$_7$·NO$_2$, C$_8$H$_7$·C$_9$NH$_6$, C$_8$H$_7$·CH:N·NHPh,
C$_8$H$_7$·CMe:N·NHPh, are incapable of forming additive compounds
with compounds of the type of NaHC(COOR)$_2$. The following deriva-
tives of cinnamic acid combine with alkylic salts of sodiomalonic acid,
C$_8$H$_7$·COOEt, (6), C$_8$H$_7$·COMe, C$_8$H$_7$·CO·NH$_2$, C$_8$H$_7$·CO·NHMe (43),
C$_8$H$_7$·CO·NHEt (44),   C$_8$H$_7$·CO·NHPh, C$_8$H$_7$·CO·NMe$_2$ (29),
C$_8$H$_7$·CO·NEt$_2$ (46), C$_8$H$_7$·CO·C$_5$NH$_{10}$ (28), C$_8$H$_7$·CO·NPh$_2$ (32), the
numbers in brackets referring to the percentages of each compound
which remain uncombined after the reaction has gone on for 6
hours.   There is apparently no fundamental difference between the
alkylic salts and the amides.   The more or less positive character of
the amine also has little influence, and tertiary and secondary amines
behave in a like manner.   E. W. W.

**Behaviour of Unsaturated Compounds towards Ethylic
Malonate.** By Paul Herrmann and Daniel Vorländer (*Chem.
Centr.*, 1899, i, 730—731 ; from *Abhand. Naturforsch. Ges. Halle*, **21**,
251—270).—The unsaturated compounds were treated with ethylic
sodiomalonate by dissolving them in alcohol together with sodium,
adding ethylic malonate, and boiling the mixture for 6 hours.

I. Unsaturated compounds not containing carbonyl. By the
action of ethylic sodiomalonate on styrene, metastyrene is formed.
Phenylnitroethylene is partly polymerised, forming a slightly soluble,
white, amorphous compound, (C$_8$H$_7$·NO$_2$)$_x$, which melts at 280°.
Stilbene, benzylidenequinaldine, cinnamaldehydephenylhydrazone, and
benzylideneacetophenonehydrazone are not attacked.

II. Unsaturated compounds containing carbonyl. Alkylic cinnamates
and cinnamamides all combine with ethylic sodiomalonate, forming the
compounds (COOEt)$_2$CH·CHPh·CH$_2$·COOEt and

(COOEt)$_2$CH·CHPh·CH$_2$·CO·NH$_2$,

which, when hydrolysed with cold sodium hydroxide solution, yield
phenylglutarocarboxylic acid and phenylglutaramidocarboxylic acid
respectively.   The former is easily soluble in water.   Phenylglutar-
amidocarboxylic acid and most of its derivatives dissolve easily in
dilute hydrochloric acid and cannot be separated from the unchanged
cinnamic acid, but by heating them with concentrated hydrochloric
acid, carbonic anhydride is eliminated and *β-phenylglutaric acid*,
C$_{11}$H$_{12}$O$_4$, is formed.   An almost quantitative yield of this acid is
also obtained by treating ethylic cinnamate with sodium (1—1½ ats.) ;
it crystallises from water in white, prismatic plates, melts at 138°, is
slightly soluble in benzene, and is only attacked by alkaline solutions

of potassium permanganate with difficulty. The *ammonium* salt crystallises in hexagonal leaflets and is stable in air. *Dimethylic β-phenylglutarate* crystallises in small, white needles or leaflets and melts at 86—87°. *β-Phenylglutaric anhydride*, $C_{11}H_{10}O_3$, prepared by the action of boiling acetic anhydride on the acid, crystallises from benzene, melts at 105°, boils at 217—219° under 15 mm. pressure, is slightly soluble in chloroform, and easily so in carbon bisulphide or boiling benzene. *β-Phenylglutarimide*, $CHPh\diagup{}^{CH_2 \cdot CO}_{CH_2 \cdot CO}\diagdown NH$, crystallises from water in small leaflets, melts at 173—174°, is insoluble in solutions of sodium carbonate, ammonia, or dilute hydrochloric acid, but dissolves in cold sodium hydroxide solution. *β-Phenylglutaranilic acid*, $COOH \cdot CH_2 \cdot CHPh \cdot CH_2 \cdot CO \cdot NHPh$, obtained by the action of aniline on the anhydride, crystallises from dilute alcohol in small needles, melts at 171°, and is easily soluble in sodium carbonate solution. The amides of cinnamic acid, with the exception of the anilide and the diphenylamide, are all soluble in hydrochloric acid. By the action of ethylic sodiomalonate on cinnamamide, a sodium salt is formed which, by the action of carbonic anhydride, yields the *compound*, $CHPh\diagup{}^{CH_2\text{———}CO}_{CH(COOEt) \cdot CO}\diagdown NH$; it crystallises from water in small needles, melts at 119°, is soluble in alkalis and in excess of hydrochloric acid, and when boiled with hydrochloric acid forms phenylglutaric acid. *Cinnamomethylamide*, $C_{10}H_{11}NO$, crystallises from water, melts at 110—111°, and is easily soluble in hot benzene or alcohol; it forms an additive compound with ethylic sodiomalonate which decomposes into phenylglutaric acid. *Cinnamodimethylamide*, $C_{11}H_{13}NO$, crystallises from water in small needles or leaflets and melts at 96°. *Cinnamoethylamide*, $C_{11}H_{13}NO$, crystallises from water and melts at 92—93°. *Cinnamodiethylamide*, $C_{13}H_{17}NO$, crystallises from very dilute alcohol in needles or prisms, melts at 66°, is very easily soluble in benzene or alcohol, and combines with bromine to form the *diethylamide* of *phenyldibromopropionic acid*, $C_{13}H_{17}NOBr_2$, which crystallises from alcohol in white prisms and melts at 127°. *Phenylglutarodiethylamidocarboxylic acid* melts at 147°, with liberation of carbonic anhydride. *Cinnamopiperidide*, $C_{14}H_{17}NO$, when treated with bromine, forms the *piperidide* of *phenyldibromopropionic acid*, $C_{14}H_{17}NOBr_2$, which crystallises from alcohol in long needles and melts and decomposes at 189°. When cinnamopiperidide is treated with ethylic sodiomalonate and the product hydrolysed, *phenylglutaropiperididocarboxylic acid*,

$$(COOH)_2CH \cdot CHPh \cdot CH_2 \cdot CO \cdot C_5NH_{10},$$
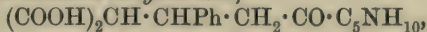
is obtained; it crystallises from water in white prisms, melts and decomposes at 146°, is easily soluble in alcohol, slightly so in benzene, is precipitated from alkaline solutions by small quantities of dilute hydrochloric acid, dissolves on the addition of more acid, but on shaking separates from the solution in a crystalline form. The *piperidide* of *phenylglutaric acid*, $COOH \cdot CH_2 \cdot CHPh \cdot CH_2 \cdot CO \cdot C_5NH_{10}$, prepared from the piperididocarboxylic acid by eliminating carbonic anhydride, crystallises from alcohol in white leaflets and melts at 120°. *Cinnamodiphenylamide* melts at 154° and combines with ethylic

sodiomalonate almost as readily as the piperidide. Cinnamanilide, when treated with ethylic sodiomalonate, forms the *anilide* of *ethylic phenylglutarate*, $CHPh<^{CH(COOEt)\cdot CO}_{CH_2———CO}>NPh$, and the *sodium* salt of an *acid anilide*. The former crystallises from alcohol in small, white needles, melts at 166°, is insoluble in ammonia or sodium carbonate solution, and by the action of cold potassium hydroxide solution forms the anilidocarboxylic acid, which, by elimination of carbonic anhydride, yields the phenylanilidoglutaric acid, $C_{17}H_{17}NO_3$, melting at 169°. The acid anilide salt is not easily obtained pure; it forms small crystals, melts and decomposes at 85—90°, by the action of boiling hydrochloric acid yields phenylglutaric acid, and when decomposed with cold potassium hydroxide solution gives the same products as the preceding compound. A third compound, the *potassium* salt of an *acid*, is obtained by hydrolysing the original alcoholic solution with cold potassium hydroxide solution; it crystallises from dilute alcohol in prisms, melts at 150—152°, and decomposes into cinnamic acid. Cinnamonitrile combines with ethylic sodiomalonate to form an oily substance which, by the action of hydrochloric acid, yields phenylglutaric acid. E. W. W.

Dialkylbenzoyl- and Dialkylbenzyl-benzoic Acids. By Albin Haller and Herm. Umbgrove (*Compt. rend.*, 1899, **129**, 90—92. Compare Abstr., 1898, i, 670).—*Dimethylamidobenzoyltetrachlorobenzoic acid*, $NMe_2\cdot C_6H_4\cdot CO\cdot C_6Cl_4\cdot COOH$, prepared by the action of dimethylaniline on tetrachlorophthalic anhydride in the presence of aluminium chloride, forms yellow scales melting at 211°, and is nearly insoluble in water, but somewhat readily soluble in alcohol or ether. It is not nitrated by a mixture of sulphuric and nitric acids. *Dimethylamidobenzoyltetrachlorobenzoic acetic anhydride*, $NMe_2\cdot C_6H_4\cdot CO\cdot C_6Cl_4\cdot COOAc$, obtained by warming a mixture of the tetrachlorobenzoic acid and dimethylaniline with acetic anhydride, crystallises in colourless scales, melts at 196°, and is soluble in benzene, but only slightly so in alcohol. The *methylic* salt, $NMe_2\cdot C_6H_4\cdot CO\cdot C_6Cl_4\cdot COOMe$, could not be prepared by the action of hydrogen chloride on a methylic alcohol solution of the acid, but was obtained by treating the mixed anhydride with the calculated amount of sodium methoxide. It forms yellow crystals and melts at 167°. The *ethylic* salt, prepared in the same way, forms yellow needles melting at 143°.

Dimethylamidobenzyltetrachlorobenzoic acid,

$$NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6Cl_4\cdot COOH,$$
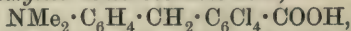
was obtained by reduction of the benzoyl acid with zinc dust and hydrochloric acid; it forms slender, white needles, melts at 215°, and is very soluble in alcohol, but less so in boiling water or ether.

Diethylamidobenzoyltetrachlorobenzoic acid,

$$NEt_2\cdot C_6H_4\cdot CO\cdot C_6Cl_4\cdot COOH,$$
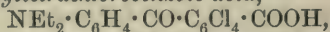
obtained in the same way as the methyl derivative, forms yellow crystals, melts at 222°, is very soluble in ethylic alcohol, but much less so in methylic alcohol or in benzene, and nearly insoluble in water; it is not nitrated by a mixture of nitric and sulphuric acids. *Diethylamidobenzoyltetrachlorobenzoic acetic anhydride* crystallises in

colourless scales, melts at 175°, and is soluble in benzene. The *methylic* salt forms yellow crystals melting at 160°, and the *ethylic* salt yellow crystals melting at 135°. H. R. Le S.

Orthotolylamidoacetic Acid. By W. HENTSCHEL (*J. pr. Chem.*, 1899, [ii], **60**, 80—84).—When purified by crystallisation from dilute sulphuric acid, orthotolylamidoacetic acid melts at 160°, and not at 149—150°; when boiled with water or mineral acids, or when heated to 220°, it loses carbonic anhydride and gives methylorthotoluidine. The glycocine forms a *hydrochloride* and a sparingly soluble *nitrate*, but not a sulphate, the base crystallising from dilute sulphuric acid; the metallic salts are much more stable. The *calcium* salt gives pure orthotoluidine when distilled. The *ethylic* salt is an oil boiling at 280°; when left for some time, it partially solidifies, forming large, transparent crystals which melt at 26°. *Dichlororthotolylamidoacetic acid* crystallises from hot dilute alcohol in needles and melts at 160—162°; when heated above the melting point, it loses carbonic anhydride and is converted into the dichloromethylorthotoluidine boiling at 258—259°. T. M. L.

Dimethylanilidophthaloylic Acid. By HEINRICH LIMPRICHT [and H. SEYLER] (*Annalen*, 1899, **307**, 305—313. Compare Abstr., 1898, i, 435; also Haller and Guyot, Abstr., 1898, i, 593 and 670).—Haller and Guyot having claimed priority to the subject investigated by the author (*loc. cit.*), a description of the work is now placed on record.

Dimethylamidohydroxybenzophenone, $NMe_2 \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot OH$, produced when dimethylanilidophthaloylic acid is heated at 260° under 20 mm. pressure, crystallises from alcohol in lustrous, white scales, and melts at 187°. When dimethylanilidophthaloylic acid is distilled with baryta, paradimethylamidobenzophenone is formed, melting at 91°.

The *chloride* of dimethylanilidophthaloylic acid,

$$NMe_2 \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot COCl,$$

obtained by treating the acid with phosphorus pentachloride suspended in carbon bisulphide, crystallises in white prisms softening at 115°; methylic alcohol converts it into methylic dimethylanilidophthaloylate, which melts at 118° (Haller and Guyot give 128°).

Nitrodimethylanilidophthaloylic acid,

$$NMe_2 \cdot C_6H_3(NO_2) \cdot CO \cdot C_6H_4 \cdot COOH + H_2O,$$

prepared by slowly adding concentrated nitric acid mixed with concentrated sulphuric acid to a solution of dimethylanilidophthaloylic acid in concentrated sulphuric acid, separates from alcohol in yellow crystals and melts at 114—115°; the *silver* salt crystallises in yellow needles and blackens in light, and the methylic salt melts at 163°.

Dimethylanilidophenylmethane, $NMe_2 \cdot C_6H_4 \cdot CH_2Ph$, produced when dimethylanilidohydrophthaloylic acid is distilled with baryta, is probably identical with the base obtained by Michler and Gradmann (Abstr., 1888, 299) on heating dimethylphenylbenzylammonium chloride; it forms colourless leaflets melting at 31°, and the *hydrochloride* begins to decompose at 115°. The *nitroso*-derivative separates from alcohol in orange-red crystals and melts at 89°. M. O. F.

Substitution of Alkyl Radicles for Sodium in Ethylic Phenylsulphonesodioacetate. By ARTHUR MICHAEL (*J. pr. Chem.*, 1899, [ii], 60, 96).—The earlier work of Comey and Michael (Abstr., 1884, 319) and of Palmer and Michael (Abstr., 1885, 986) on the substitution of alkyl radicles for sodium in the compound

$$SO_2Ph\cdot CHNa\cdot COOEt,$$
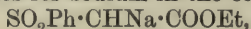
has been repeated and confirmed. The statements of Otto and Rössing (Abstr., 1889, 994) to the effect that this substitution does not take place are therefore without foundation. T. M. L.

Mercuriphenyl Sulphide and Thiosulphate. By LEONE PESCI (*Gazzetta*, 1899, 29, i, 394—399).—*Mercuriphenyl sulphide*, $(PhHg)_2S$, obtained by the action of hydrogen sulphide or an alkali sulphide on a solution of mercuriphenyl acetate in ammoniacal ammonium acetate, is a white, amorphous powder insoluble in water or alcohol, but soluble in chloroform, giving a solution which rapidly changes, a yellow powder being deposited. Hot fuming hydrochloric acid dissolves it, but the cold dilute acid blackens it, hydrogen sulphide being evolved in both cases. Heated at 108°, it decomposes and becomes black, and when boiled in a reflux apparatus with alcohol, it is split up into mercuric sulphide and mercury diphenyl. It is soluble in cold carbon bisulphide, and the solution deposits first colourless, silky needles and afterwards a yellowish substance which only partially redissolves in carbon bisulphide, and is shown to be *mercuriphenyl thiocarbonate*, $(PhHg)_2CS_3$. This compound is insoluble in water or alcohol, slightly soluble in ether or benzene, more so in chloroform, and is completely dissolved by hot fuming hydrochloric acid. At 108°, it blackens, mercuric sulphide being formed and carbon bisulphide evolved, and when heated with benzene, it decomposes rapidly with the production of mercuric sulphide and mercury diphenyl.

Mercuriphenyl thiosulphate, $(PhHg)_2S_2O_3$, prepared by adding a solution of 1 mol. of sodium thiosulphate to a solution of 2 mols. of mercuriphenyl acetate in ammoniacal ammonium acetate, is a white, amorphous precipitate insoluble in the ordinary solvents, but soluble in concentrated hydrochloric acid with the evolution of sulphurous anhydride and separation of sulphur. It is apparently unchanged when heated at 200°, and dissolves readily in aqueous sodium thiosulphate, giving a solution which, on standing, deposits mercury diphenyl. T. H. P.

Chemistry of Lignite Tar. By EUGEN OEHLER (*Zeit. angew. Chem.*, 1899, 561—563).—The alkaline solution obtained in the extraction of creosote from the crude oil by means of aqueous caustic soda of 40° Beaumé (sp. gr. 1·375) contains, in solution, some oil (" neutral creosote ") which is liberated upon dilution with water. This oil has been examined and found to have essentially the same composition as the original oil; in addition to unsaturated substances removable by strong sulphuric acid, nonane, decane, toluene, metaxylene, and naphthalene were detected in it. Much the same substances were also detected in neutral creosote from paraffin oil; in this, undecane was found. Attention was also paid to the bases extracted

from the crude oil with sulphuric acid, and aniline was detected amongst these.

A new *hydrocarbon*, $C_{16}H_{18}$, which melts at 117°, boils at 300—303°, and forms a red *picrate*, $C_{16}H_{18},C_6H_3N_3O_7$, melting at 154°, has been isolated from a press-oil, poor in paraffin. A middle fraction of this was distilled several times until about 80 per cent. passed over at 290—320°. In this fraction, about 8 per cent. of its weight of picric acid was dissolved with the aid of heat, and the picrate which separated on cooling was washed with light petroleum and decomposed with ammonia; the fraction contained about 0·5 per cent. of the hydrocarbon in question.   C. F. B.

Derivatives of Unsymmetrical Tetramethyldiamidodiphenyl-ethane. By AUGUSTE TRILLAT (*Compt. rend.*, 1899, **128**, 1404—1406. Compare this vol., i, 615).—The following derivatives of unsymmetrical tetramethyldiamidodiphenylethane are described: The *hydrochloride*, $C_{18}H_{24}N_2,2HCl$, forms a white, crystalline powder decomposing at 225°; it is soluble in alcohol or water, but almost insoluble in acetone; the *dihydrogen sulphate*, $C_{18}H_{24}N_2,2H_2SO_4$, is hygroscopic and melts at 188—189°; the *acetate* crystallises in long needles which redden on exposure to air. The *ethobromide*, $C_{18}H_{24}N_2,2EtBr$, melts and decomposes at 224—225°, and is soluble in alcohol or water, but insoluble in acetone; the *ethiodide*, $C_{18}H_{24}N_2,2EtI$, decomposes at 228—230°. Unstable *compounds*, $C_{18}H_{21}Br_3N_2$ and $C_{18}H_{21}I_3N_2$, are obtained by the action of bromine and iodine respectively on the base dissolved in acetic acid. The *dinitro*-derivative, $C_{18}H_{22}N_2(NO_2)_2$, prepared by adding cold fuming nitric acid to an acetic acid solution of the base, crystallises in pale yellow prisms melting at 195—196°; polynitro-derivatives are obtained when the nitration is performed in the presence of sulphuric acid. Paranitrodimethylaniline is produced when sodium nitrite is added to a solution of the base in cold acetic acid.   G. T. M.

Constitution of $\beta\beta$-Dinaphthol. By R. FOSSE (*Bull. Soc. Chim.*, 1899, [iii], 21, 650—653).—The constitution of $\beta\beta$-dinaphthol (this vol., i, 529) is most probably represented by the formula

$$\frac{CH \cdot C(OH)}{C_6H_4 - CH} {>} C \cdot C {<} \frac{C(OH) \cdot CH}{CH - C_6H_4},$$
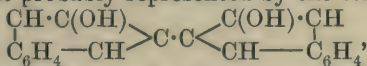
which explains the formation of $\alpha\alpha$-dinaphthyl when $\beta\beta$-dinaphthol is heated with zinc dust, and its conversion into ortho-β-hydroxy-naphthoylbenzoic acid by oxidation with potassium permanganate. It is in accordance with the ready transformation of $\beta\beta$-dinaphthol into dinaphthylenic oxide, and into an imine instead of a diamine, and also with the fact that no aldehydic compound could be obtained by Reimer and Tiemann's reaction.   N. L.

Some New Derivatives of $\beta\beta$-Dinaphthol. By R. FOSSE (*Bull. Soc. Chim.*, 1899, [iii], 21, 655—659).—$\beta\beta$-Dinaphthol reacts with propionic chloride to form a *dipropionate*, $C_{20}H_{12}(O \cdot CO \cdot CH_2Me)_2$, which crystallises from alcohol in transparent needles melting at 105°. The *dibutyrate*, $C_{20}H_{12}(O \cdot CO \cdot CH_2 \cdot CH_2Me)_2$, prepared in a similar manner from butyric chloride, crystallises from alcohol in short, slender needles melting at 207°. The *phthalate*, $C_{20}H_{12} {<} \frac{O \cdot CO}{O \cdot CO} {>} C_6H_4$,

is a white, crystalline substance which melts and decomposes at 215°. Unsuccessful attempts were made to prepare a phthalein by the action of phthalic anhydride on $\beta\beta$-dinaphthol. *Dinaphthylic isopropylic ether*, $C_{20}H_{12}(O\cdot CHMe_2)_2$, is crystalline and melts at 150°. *Dibromo-$\beta\beta$-dinaphthol*, $C_{20}H_{12}Br_2O_2$, obtained by adding the theoretical amount of bromine to a solution of $\beta\beta$-dinaphthol in acetic acid, melts at 155°, and is very soluble in alcohol and ether. Its *potassium* derivative crystallises in colourless, striated prisms, and the *sodium* derivative is a crystalline powder ; these compounds rapidly turn brown on exposure to air, but are more stable than the corresponding alkali derivatives of $\beta\beta$-dinaphthol. *Dichlorodinaphthylene oxide*, $C_{20}H_{10}Cl_2O$, obtained by heating a solution of $\beta\beta$-dinaphthol in carbon bisulphide with sulphuryl chloride, crystallises in yellow needles melting at 165°. It gives a violet coloration with sulphuric acid, and is isomeric with the substance, melting at 245°, produced by the action of phosphorus pentachloride on dinaphthylenic oxide.   N. L.

Action of Aldehydes and Aldehydic Chlorides on $\beta\beta$-Dinaphthol: Acetals. By R. FOSSE (*Bull. Soc. Chim.*, 1899, [iii], 21, 653—655. Compare this vol., i, 529).—$\beta\beta$-Dinaphthol does not enter into reaction with aldehydes in the presence of sulphuric acid, zinc chloride, or hydrogen chloride, but when heated with aldehydic chlorides, $R\cdot CHCl_2$, and alcoholic potash or sodium ethoxide, compounds analogous to acetal are obtained in nearly theoretical quantity. *Dinaphthyl benzylidenic ether*, $C_{20}H_{12}{<}^O_O{>}CHPh$, from $\beta\beta$-dinaphthol and benzylidenic chloride, is crystalline, and melts at 128°. *Dinaphthyl ethylidenic ether*, $C_{20}H_{12}{<}^O_O{>}CHMe$, from $\beta\beta$-dinaphthol and ethylidenic chloride, is a crystalline substance melting at 112°. These compounds are decomposed by dilute acids and concentrated alkalis, with the formation of $\beta\beta$-dinaphthol and benzoic and acetic aldehydes respectively.   N. L.

Diphenylanthrone Derivatives. By L. TÉTRY (*Compt. rend.*, 1899, 128, 1406—1407. Compare Abstr., 1898, i, 483).—*Methoxydiphenylanthrone*, $OMe\cdot C_6H_4\cdot CPh{<}^{C_6H_4}_{C_6H_4}{>}CO$, obtained by condensing anisoil with chlorophenylanthrone in carbon bisulphide solution in the presence of aluminium chloride, crystallises in colourless prisms melting at 180—181° ; it is soluble in the ordinary organic solvents, and, like other compounds of this group, develops a yellow coloration with concentrated sulphuric acid. *Ethoxydiphenylanthrone* melts at 159—160°, and in properties resembles its lower homologue ; it separates from benzene in colourless prisms containing 1 mol. of this solvent.

Dimethylamidodiphenylanthrone, $NMe_2\cdot C_6H_4\cdot CPh{<}^{C_6H_4}_{C_6H_4}{>}CO$,   is prepared by substituting dimethylaniline for anisoil in the condensation. The base crystallises in transparent, yellow prisms melting at 215° ; its salts are dissociated by water. *Diethylamidodiphenylanthrone* crystallises from toluene in transparent, yellow, dichroic prisms which contain $\frac{1}{2}$ mol. of toluene ; it melts at 194—195°. The colour of these bases is less intense than that of the corresponding dialkylamido-

anthraquinones, diphenylanthrone, which contains only one carbonyl chromophore, being a weaker chromogen than anthraquinone.

G. T. M.

Dimethyldianthracene, a Polymeride of β-Methylanthracene. By WILLIAM R. ORNDORFF and H. A. MEGRAW (*Amer. Chem. J.*, 1899, **22**, 152—157).—When β-methylanthracene, suspended in benzene, is exposed to the action of sunlight, it is rapidly polymerised into *dimethyldianthracene*, $(C_{15}H_{12})_2$, just as anthracene, under similar conditions, gives rise to dianthracene (Orndorff and Cameron, Abstr., 1896, i, 176) ; the product crystallises from toluene in small, probably orthorhombic, crystals and melts at 228—230°, decomposing partially into β-methylanthracene. Its molecular weight was determined by the boiling point method, using toluene and pyridine as solvents. Unlike β-methylanthracene, it is non-fluorescent, and does not form a compound with picric acid. It is very sparingly soluble in all the ordinary solvents, but when boiled for a long period with anisoil or metaxylene, becomes partially soluble owing to conversion into β-methylanthracene.

W. A. D.

Optical Rotation of Pinene Hydrochloride. By JOHN H. LONG (*J. Amer. Chem. Soc.*, 1899, **21**, 637—642).—Pinene hydrochloride melts at 131°, and not at 125° as stated by Pesci (Abstr., 1889, 158) and others. Various values have been given by different authorities for the specific rotatory power of the hydrochloride (compare Berthelot *Ann. Chim. Phys.*, 1854, [iii], **40**, 5; Flawitzky, *Ber.*, 1882, **15**, 5; Marsh and Gardner, Trans., 1891, **59**, 725; Pesci, *loc. cit.* ; Wallach and Conrady, Abstr., 1889, 1072). The different values—from 0° to +30°—are due to the fact that the hydrocarbon employed by the different authorities contained varying amounts of *d*- and *l*-pinene. From experiments made by the author, it appears that the hydrochloride of *l*-pinene has a higher rotatory power than *l*-pinene, whereas the hydrochloride from *d*-pinene has a slightly lower rotatory power than *d*-pinene. J. J. S.

Crystallographic Relations of Optically Active Substances and their Racemic Compounds [Pinonic Acids]. By ANDREAS FOCK (*Zeit. Kryst. Min.*, 1899, **31**, 479—483).—Optically active substances may be divided into three groups: (1) those with no racemic compounds, the two antipodes crystallising separately from the mixed solution ; for example, asparagine and *cis-π*-camphanic acid ; (2) those in which the antipodes unite in constant proportions to form a racemic compound, for example, tartaric acid and tartrates ; (3) those in which the antipodes unite in varying proportions to form numerous racemic or pseudoracemic compounds, for example, limonene tetrabromide and brucine valerate. Between groups (1) and (2) there is a connecting link, thus the racemate, $(C_4H_4O_6NaNH_4)_2 + 2H_2O$, is formed from the two tartrates above 27°, whilst below this temperature the two antipodes crystallise separately. A connecting link between groups (2) and (3) is now described.

The optically active pinonic acid crystallises in tetragonal pyramids, and the two antipodes have the same form $[a : c = 1 : 1\cdot12757]$. Circular polarisation could not be observed in the imperfect crystals, but their solutions show wide variations in the rotatory power ; in the lævo-acid, $[a]_D$ reaches 20°, and in the dextro-acid, $[a]_D$ may reach 130°.

This variation is to be explained by the capability of the two modifications mixing together as isomorphous substances. The racemic compound of the two active pinonic acids forms tabular, monoclinic crystals [$a : b : c = 0\cdot6445 : 1 : 0\cdot5585$; $\beta = 76° \; 8'$]. Solutions of these crystals show rotations up to [a]$_D = 10°$. The two active compounds must therefore, to a certain extent, crystallise isomorphously with the racemic compound, giving a passage between groups (2) and (3). This would be expected to take place in the pseudo-racemic compounds, the crystalline forms of which differ only slightly from those of the corresponding active substances.

Amongst inorganic salts, group (2) is represented by double salts and (3) by isomorphous mixtures, and there are also analogous connecting links between the groups.   L. J. S.

Amidocampholenes. By EDMOND E. BLAISE and G. BLANC (*Compt. rend.*, 1899, **129**, 106—108).—β-Campholenamide,

$$CH_2 \begin{matrix} CMe_2 \cdot CMe \\ \| \; \| \\ CH_2 - C \cdot CH_2 \cdot CO \cdot NH_2 \end{matrix},$$
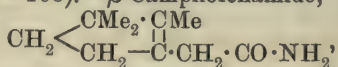
on oxidation with potassium hypobromite, gives *β-amidocampholene*,

$$CH_2 \begin{matrix} CMe_2 \cdot CMe \\ \| \; \| \\ CH_2 - C \cdot CH_2 \cdot NH_2 \end{matrix}.$$

This is a colourless liquid, has an ammoniacal odour, and boils at 185° under atmospheric pressure ; it has a sp. gr. 0·8778 at 15°, and a molecular refraction n_D 44·83. The *hydrochloride* crystallises in long needles melting at 194—195°, the *platinochloride* decomposes above 200°, the *picrate* melts at 228—229°, and the *oxamide* at 111—112°. By interaction with potassium cyanate, the hydrochloride forms a substituted *carbamide* melting at 108—109°.

a-Campholenamide, with potassium hypobromite, gives *a-amidocampholene*, $CH_2 \begin{matrix} CMe_2 \cdot C : CH_2 \\ \| \\ CH_2 - CH \cdot CH_2 \cdot NH_2 \end{matrix}.$ This boils at 185° ; has a sp. gr. 0·8795 at 15°, and a molecular refraction n_D 44·88. The *hydrochloride* forms small prisms melting at 253°, the *picrate* melts at 219°, and the *oxamide* crystallises in needles fusing at 131°. With potassium cyanate, a substituted *carbamide* is formed melting at 119—120°.

a- and β-Amidocampholenes, on reduction, should both give an amidodihydrocampholene identical with that prepared by one of the authors from isolauronolic nitrile (Blanc, *Bull. Soc. Chim.*, 1899, [iii], **21**, 322). Attempts were therefore made to obtain this from each, but instead of the amidodihydrocampholene, a base was obtained the boiling point of which was much higher than that of the compound sought.   H. R. LE S.

Cascara Sagrada. By LEPRINCE (*Compt. rend.*, 1899, **129**, 60—61).—If cascara sagrada, the bark of *Rhamnus purshiana*, is extracted with 5 per cent. aqueous soda and the liquid acidified, a precipitate is obtained which consists chiefly of chrysarobin, chrysophanic acid, and emodin. Details of the separation and identification of these substances are given in the paper.   N. L.

Aloins. By EUGÈNE LÉGER (*Compt. rend.*, 1899, **128**, 1401—1403. Compare Abstr., 1898, i, 445 ; this vol., i, 157).—Finely ground Natal aloes were digested with cold acetone to remove resinous matters, and

then extracted with boiling methylic alcohol and filtered ; the filtrate, on cooling, deposited yellow, lamellar crystals which were separated into two constituents by fractional crystallisation from the same solvent.

Nataloin, $C_{16}H_{18}O_7$, the more soluble compound, forms pale yellow scales less soluble in methylic alcohol than barbaloin, and insoluble in hot water or ether. Like barbaloin, it possesses a phenolic character, and dissolves in alkaline solutions, from which it is re-precipitated by carbonic anhydride. It dissolves in ammonia or pyridine, but combines with acids less readily than barbaloin. Acetic chloride forms with it a small quantity of a crystalline *acetyl* derivative separating in octahedra and in scales, but the principal product is a yellow, amorphous substance very soluble in ether. *Tribenzoyl-nataloin,* $C_{16}H_{15}O_7Bz_3$, obtained by the action of benzoic chloride on nataloin in pyridine solution, forms a yellow, tumid mass very soluble in ether or alcohol, but insoluble in water or dilute solutions of the alkalis ; it is devoid of bitter taste. The *tetrabenzoyl* derivative, $C_{16}H_{14}O_7Bz_4$, obtained by heating the aloin with benzoic chloride in sealed tubes at 100°, separates from alcohol in yellow, amorphous granules.

Homonataloin, $C_{15}H_{16}O_7$, the less soluble constituent of the crude aloin, separates from methylic alcohol in nodular masses of yellow lamellæ ; its *acetyl* derivative is amorphous. The *tri-* and *tetra-benzoyl* derivatives, $C_{15}H_{13}O_7Bz_3$ and $C_{15}H_{12}O_7Bz_4$ are obtained in brick-red granules.

These aloins develop a green coloration with sulphuric acid and manganese dioxide or potassium dichromate, and a violet with a soda solution containing ammonium persulphate ; the latter colour dyes silk, but cannot be fixed on mordanted cotton. These colour reactions distinguish the aloins of Natal aloes from barbaloin.   G. T. M.

Brazilin and Hæmatoxylin. By JOSEF HERZIG (*Monatsh.*, 1899, **20**, 461—466. Compare this vol., i, 381).—The author criticises the conclusions of Feuerstein and v. Kostanecki (this vol., i, 538), and of Gilbody and Perkin (Proc., 1899, **15**, 75), with regard to the formulæ of brazilin and hæmatoxylin.   R. H. P.

Gossypol, a Constituent of Cotton-seeds. By LEO MARCH-LEWSKI (*J. pr. Chem.*, 1899, **60**, 84—90).—When the phenolic con-stituents of cotton-seed oil are purified by repeated fractionation from acetic acid solution, a crystalline product is obtained which can be further purified by crystallisation from a mixture of alcohol and dilute acetic acid ; this substance, to which the name of *gossypol* is given, has a composition corresponding fairly well with that required for the formula $C_{13}H_{14}O_4$. Gossypol crystallises in glistening, golden scales, melts at 188°, dissolves readily in alcohol, benzene, chloroform, ether, acetone, or acetic acid, but not in water. Sulphuric acid dissolves it with a beautiful, cherry-red coloration, similar to that observed with impure cotton-oils. Alkalis give a yellow solution, which soon be-comes violet and then gradually loses its colour ; the violet colour is developed immediately when hydrogen peroxide is added to the alkaline solution. Alkaline solutions of gossypol reduce both Fehling's solution and ammoniacal silver nitrate. An alcoholic solu-

tion gives a dark green coloration with ferric chloride, which becomes dark reddish-brown on adding alkalis. The acetyl and benzoyl derivatives are very soluble in organic solvents, and were not obtained in crystalline form; bromine and nitric acid also act on gossypol, but definite products were not isolated. Gossypol is not a glucoside. An analysis of the *lead* salt indicates the presence of two hydroxyl groups. Gossypol gives a grey shade with iron mordants.　　　　T. M. L.

Fatty Oil of Quince Seeds. By ROBERT HERRMANN (*Arch. Pharm.*, 1899, **237**, 358—368).—Seeds of the quince (*Cydonia vulgaris*) were ground, dried carefully, and extracted with ether, chloroform, or light petroleum; fresh seeds yielded 15·3 per cent. of oil. The oil was yellow and had a faint odour of oil of almonds; it had a solidification point $-13·5°$, sp. gr. 0·922 at 15°, solubility 4·15 parts in 100 of 95 per cent. alcohol, index of refraction 1·47248 for green, 1·47292 for red, viscosity 16·4 at 17° (by Schubler's method, comparing its velocity of efflux with that of water); it was optically inactive and showed obscure absorption bands in the blue and violet. 1 gram neutralised 31·7 milligrams KOH in the cold ("acid number"), 181·7 on heating ("Koettstorfer's" or "saponification number"); 5 grams contained volatile acids soluble in water sufficient to neutralise 0·508 c.c. $N/10$ KOH solution ("Reichert-Meissl number"); it contained 95·2 per cent. of fatty acids insoluble in water ("Hehner's number"), and united with 113 per cent. of iodine ("Hübl's iodine number").

By hydrolysis of the oil with lead oxide, glycerol was obtained to the extent of 4·1 per cent. A larger quantity of the oil was hydrolysed with caustic soda, and the acids converted into calcium salts, which were then treated with ether. From the calcium salt soluble in ether, a liquid acid was obtained, and purified by conversion into its ethylic salt and fractional distillation of the latter. This acid has a sp. gr. 0·8931 and composition $OH·C_{17}H_{32}·COOH$; its *ethylic* salt boils at 223—226° under 7·5 mm. pressure; an anhydrous *barium* salt, melting at 79°, and a *monacetyl* derivative were prepared; a *dibromide*, $C_{18}N_{34}O_3Br_2$, was also prepared, and the acid was found to darken in the air, absorbing oxygen. From the calcium salt insoluble in ether, a mixture of solid acids was obtained from which two were separated by crystallisation from 70 per cent. alcohol; these were myristic acid, the main product, and a small amount of an acid which melts at 42°, contains C 75·1 and H 12·1 per cent., and is possibly an isomeride of pentadecylic acid.　　　　C. F. B.

Pectin from Quince. By JAVILLIER (*J. Pharm.*, 1899, [vi], **9**, 163—166 and 513—515).—This pectin is strongly dextrorotatory, $[a]_D = 188·2°$. On hydrolysis with dilute sulphuric acid, it yields arabinose; when treated with nitric acid, it gives mucic acid, and with diastase from germinated barley it behaves exactly like the pectin obtained from gentian and the gooseberry (Bourquelot and Hérissey, Abstr., 1898, i, 607; this vol., i, 653).　　　　H. R. LE S.

Chlorophyll. By LEO MARCHLEWSKI (*J. pr. Chem.*, 1899, **60**, 91—95).—A controversial reply to Kohl (this vol., i, 228).
　　　　　　　　　　T. M. L.

Action of Ethylic Diazoacetate on Pyrroline, 1-Methyl-pyrroline and some Indoles. By ANTONIO PICCININI (*Gazzetta*, 1899, **29**, i, 363—371).—1-*Methylpyrrylacetic acid*, $C_4NH_3Me \cdot CH_2 \cdot COOH$, obtained by hydrolysing the product formed by the action of ethylic diazoacetate on 1-methylpyrroline or pyrroline, crystallises from light petroleum in colourless leaflets with a nacreous lustre, and melts at 113—114°; it is very soluble in water, alcohol, or ether, slightly so in cold light petroleum, and tends to become red in the air. It does not give the pyrroline reaction with isatin, nor does it colour cold concentrated sulphuric acid, but gives immediately an intense red coloration to a pine shaving moistened with hydrochloric acid. The salts formed with the alkali and alkaline-earth metals are very soluble in water; the *lead* salt forms a white precipitate, and the *silver* salt colourless, very slightly soluble flocks which change rapidly even in the cold, and when suspended in water and heated are instantly reduced; the *mercury* salt is deposited as a bulky, colourless precipitate which becomes red, slowly in the cold and more rapidly on heating.

1'-*Methylindole*-3'-*acetic acid*, $MeN{<}^{-CH}_{C_6H_4}{>}C \cdot CH_2 \cdot COOH$, prepared from 1'-methylindole and ethylic diazoacetate, forms colourless prisms melting at 128—129°, and is very soluble in benzene or alcohol, less so in boiling water, and only very slightly in light petroleum. The *silver* salt, $C_{11}H_{10}NO_2Ag$, forms a colourless, microcrystalline precipitate readily decomposed by heating, and the *picrate* is deposited in garnet-red, silky needles melting at 173—174°. On heating the acid at 200—220°, it is converted quantitatively into 1' : 3'-dimethylindole, carbonic anhydride being eliminated.

2'-Methylindole and ethylic diazoacetate give rise to the 2'-methyl-indole-3'-acetic acid, melting at 204°, obtained by Fischer (Abstr., 1887, 806) from the phenylhydrazone of lævulinic acid.　　T. H. P.

Action of Benzylideneaniline on Pyruvic Acid and its Ethylic Salt. By KARL GARZAROLLI-THURNLACKH (*Monatsh.*, 1899, **20**, 480—487).—The principal product of the action of benzylidene-aniline on pyruvic acid or on its ethylic salt is the compound $C_{22}H_{18}N_2O$, first obtained by Doebner (Abstr., 1887, 504) by the action of aniline on a mixture of pyruvic acid and benzaldehyde; this the author regards as the 4-*anil* of 1 : 2-diphenyl-4 : 5-diketotetrahydro-pyrroline. It is only when the reaction occurs in dilute solution that small quantities of diphenyldiketodihydropyrroline are formed (compare Schiff, Abstr., 1898, i, 490).　　R. H. P.

Action of Hydrazine Hydrate on Acenaphthenequinone. By LUDWIG BEREND and JOACHIM HERMS (*J. pr. Chem.*, 1899, [ii], **60**, 1—25. Compare Curtius and Thun, Abstr., 1891, 1355).—*Peri-naphthoylhydrazimethylene*, ${}^{CO-}_{C_{10}H_6}{>}C{<}^{NH}_{NH}$, produced by the action of hydrazine hydrate on acenaphthenequinone, melts at 140°, and gives off nitrogen when heated to 165°. It crystallises from dilute alcohol in needles of a yellow to brown colour, dissolves readily in hot alcohol and in benzene, ether, or chloroform, but less readily in hot water,

from which it separates unchanged on cooling. A yellow substance which is insoluble in alcohol and does not melt at 270° is also produced in the reaction. *Perinaphthoylmethylenemetanitroisobenzalazine,* $\mathrm{CO{-}{>}C{<}\!\!\begin{smallmatrix}N\\N\end{smallmatrix}\!\!{>}CH\cdot C_6H_4\cdot NO_2}$, with $C_{10}H_6$, produced by condensation of the hydrazimethylene with metanitrobenzaldehyde, crystallises from nitrobenzene in microscopic, straw-yellow needles, melts and decomposes at 253°, dissolves to some extent in boiling chloroform, but not in alcohol or ether. *Perinaphthoylazomethylene,* prepared by oxidising the hydrazo-compound with mercuric oxide, separates from light petroleum in orange to reddish-yellow needles and fan-shaped crystals, melts at 79—80°, and loses nitrogen at 120°; it dissolves easily in alcohol, ether, chloroform, benzene, or acetic acid, less readily in light petroleum, and is quite insoluble in water; it explodes when mixed with concentrated sulphuric acid, or when rapidly heated above the melting point. *Perinaphthoyldibromomethylene,* $\mathrm{C_{10}H_6{<}\!\!\begin{smallmatrix}CO\\CBr_2\end{smallmatrix}}$, separates from light petroleum in stout prisms and rhombic crystals, and melts at 160—161°. *Perinaphthylenehydrazimethylenemetanitroisobenzalazine* (?), $\mathrm{\begin{smallmatrix}NH\\NH\end{smallmatrix}\!\!{>}C{-}\!\!\underset{C_{10}H_6}{}\!\!{-}C{<}\!\!\begin{smallmatrix}N\\N\end{smallmatrix}\!\!{>}CH\cdot C_6H_4\cdot NO_2}$, prepared by the action of hydrazine hydrate on the azine described above, crystallises in yellow tablets and melts at 215—216° with liberation of nitrogen.

Perinaphthylenedihydrazimethylene, $\mathrm{\begin{smallmatrix}NH\\NH\end{smallmatrix}\!\!{>}C{-}\!\!\underset{C_{10}H_6}{}\!\!{-}C{<}\!\!\begin{smallmatrix}NH\\NH\end{smallmatrix}}$, obtained by the action of hydrazine hydrate on the hydrazimethylene derivative, crystallises from dilute alcohol in yellow needles, melts at 192°, dissolves readily in hot alcohol or chloroform, less readily in ether or hot water, and is insoluble in cold water. *Perinaphthylenedimetanitroisobenzalazine* (?),

$$\mathrm{NO_2\cdot C_6H_4\cdot CH{<}\!\!\begin{smallmatrix}N\\N\end{smallmatrix}\!\!{>}C{-}\!\!\underset{C_{10}H_6}{}\!\!{-}C{<}\!\!\begin{smallmatrix}N\\N\end{smallmatrix}\!\!{>}CH\cdot C_6H_4\cdot NO_2,}$$

crystallises from chloroform in glistening, hexagonal tablets and prisms, melts at 246°, dissolves readily in hot nitrobenzene, and slightly in boiling chloroform, but not at all in alcohol or ether.

Perinaphthoylmonochloromethylene, $\mathrm{C_{10}H_6{<}\!\!\begin{smallmatrix}CO\\CHCl\end{smallmatrix}}$, prepared by the action of hydrogen chloride on perinaphthoylazomethylene, crystallises from chloroform in microscopic, colourless needles, and melts at 109—110°.

The paper contains a summary of previous work on the action of hydrazine hydrate on aldehydes and ketones, and a comparison between the behaviour of acenaphthenequinone and benzil towards this agent (Curtius and Thun, *loc. cit.*). T. M. L.

Paratolylpseudazimidoquinoline. By CONRAD WILLGERODT and HEINRICH DAUNER (*J. pr. Chem.,* 1899, **60**, 72—79).—*Paratolyl-*

pseudazimidonitrobenzene, $C_6H_4Me \cdot N \underset{N}{\overset{N}{<}} > C_6H_3 \cdot NO_2$, prepared by the action of sodium hydrogen carbonate on paratolylhydrazine and α-dinitrochlorobenzene in boiling alcoholic solution, crystallises from alcohol in yellow needles, and melts at 165—166°. *Paratolylpseudazimidoamidobenzene* crystallises from alcohol in greenish needles and melts at 212—213°.

Paratolylpseudazimidoquinoline, $C_6H_4Me \cdot N \underset{N}{\overset{N}{<}} > C_9NH_5$, [N : N = 3 : 4 or 2 : 3], melts at 184°, crystallises from alcohol in yellow needles, dissolves fairly readily in ether or chloroform, and to some extent in hot water or acetic acid. The *hydrochloride*, $C_{16}H_{12}N_4, HCl$, crystallises from alcohol in yellowish-white, glistening needles, and melts and decomposes at 224°; the *nitrate* separates from alcohol in short, brownish needles and melts at 192°; the *sulphate* crystallises from alcohol in brown needles and melts and decomposes at 248°. The *dichromate* crystallises in splendid, orange-yellow needles, but blackens when exposed to light. The *acetate* forms grey, glistening, pointed leaflets and melts at 180°. The *platinochloride*, $(C_{16}H_{12}N_4)_2, H_2PtCl_6$, and the *mercurichloride* crystallise in microscopic needles. The *methiodide* crystallises from hot water in splendid, golden-yellow needles and melts at 268°; the *ethiodide* crystallises in flat, golden needles. The *ethobromide* melts at 203°, and is only very slightly soluble in hot water, but crystallises from alcohol in short, grey leaflets. The *methochloride* separates from water in a white, crystalline mass, dissolves readily in alcohol, and melts at 225°; the *ethochloride* is extremely soluble in alcohol and water. The *methodichromate*, $(C_{16}H_{12}N_2Me)_2Cr_2O_7$, crystallises from water in fine, orange-yellow needles and dissolves readily in alcohol; its temperature of decomposition is very high. T. M. L.

Diazoles from Carbazinic Acids. By MAX BUSCH (*J. pr. Chem.*, 1899, [ii], **60**, 25—55).—The dithiocarbazinic acids, $R \cdot NH \cdot NH \cdot CS \cdot SH$ or $R \cdot NH \cdot N{:}C(SH)_2$, as well as their metallic and ethereal salts, condense with various substances to form ring compounds containing two atoms of nitrogen. Carbon bisulphide gives dithiodiazolonethiols, $R \cdot N \underset{CS \cdot S}{\overset{N=C \cdot SK}{<}}$; carbonyl chloride gives thiodiazolonethiols, $R \cdot N \underset{CO \cdot S}{\overset{N=C \cdot SH}{<}}$; aldehydes and certain ketones give thiodiazolinethiols, $R \cdot N \underset{CR^1R^{11} \cdot S}{\overset{N=C \cdot SH}{<}}$, which can also be prepared by reducing the dithiodiazolonethiols; acid chlorides give isodithiodiazolones, $R \cdot N \underset{CR^1 \cdot S}{\overset{N-CS}{<}}$. The condensation products of carbon bisulphide with dithiocarbazinic acid, and with methyldithiocarbazinic acid are described below, the other series of compounds being described in a later paper.

I [By E. ZIEGELE. Compare Curtius and Heidenreich, Abstr., 1894, i, 166.]—The *dimethylic ether* of *thiodiazoledithiol*, $S \underset{C(SMe){:}N}{\overset{C(SMe){:}N}{<}}$

crystallises from benzene in long, glistening needles, melts at 136°, and dissolves readily in the ordinary organic solvents. When oxidised with iodine, the dithiol yields a *bisulphide*, $S_2\left(C<^{N\cdot N}_{S\cdot C\cdot SH}\right)_2$, which separates from dilute methylic alcohol in lemon-yellow, glistening crystals, melts at 175°, and dissolves readily in boiling ethylic or methylic alcohol, or in ethylic acetate. Ferric chloride gives the same bisulphide, together with a *polysulphide*, $(C_2N_2S_3)_x$, which was obtained as an insoluble, white powder melting at 207° to a yellow oil, and was reduced again to the dithiol by alcoholic potash or alcoholic ammonia. The *potassium* salt of the bisulphide, $C_4N_4S_6K_2$, forms lemon-yellow needles and melts at 205°; the action of alcoholic potash on the bisulphide at the ordinary temperature instead of at that of a freezing mixture, however, brings about the reduction of the bisulphide to the potassium salt of the dithiol. The *dibenzylic ether*, $C_{18}H_{14}N_4S_6$, forms white, felted needles and melts at 109°. When oxidised with potassium permanganate, the dithiol gives *potassium thiodiazoledi-sulphonate*, $S<^{C(SO_3K):N}_{C(SO_3K):N}$, which crystallises from water in large, glistening prisms. It was not found possible to produce either thiodiazole, $S<^{CH:N}_{CH:N}$, or dihydroxythiodiazole, $S<^{C(OH):N}_{C(OH):N}$, by elimination of the sulphonic groups, but hydrolysis with hydrochloric acid gave *potassium oxythiodiazolesulphonate*, $S<^{C(OH)=N}_{C(SO_3K):N}$.

The action of ammonia on the bisulphide of thiodiazoledithiol appears to give rise to the ammonium salts of the dithiol and of thiodiazolethiolsulphamine, $S<^{C(SH)=N}_{C(S\cdot NH_2):N}$, but these could not be isolated. The dibenzylic ether of the bisulphide acts similarly, but the hydrosulphamine derivative could not be isolated; the *monobenzylic ether*, $S<^{C(SH)=N}_{C(S\cdot CH_2Ph):N}$, which is formed as the other product of the action, melts at 131°, dissolves readily in alkalis, and in alcohol, chloroform, ether, or benzene, and crystallises well from dilute alcohol.

The action of aniline on the bisulphide gives rise to the original bisulphide together with *amidobenzene-thio-thiodiazolethiol* (mercapto-thiodiazoleamidophenylsulphide), $SH\cdot C<^{N\cdot N}_{S}>C\cdot S\cdot C_6H_4\cdot NH_2$; this crystallises from 50 per cent. alcohol in colourless needles, melts at 187°, dissolves readily in alcohol, ether, or hot water, but only slightly in chloroform or benzene; it smells of an isonitrile when heated with chloroform and alcoholic potash, gives a diazo-compound with nitrous acid, and possesses both acid and basic properties. The *hydrochloride* crystallises in colourless needles and melts at 206°. The *diazo-chloride* melts with frothing at 133° and condenses with β-naphthol to a red dye which melts at 222°. It is probable that the first product of the action of aniline on the bisulphide is the hydrosulphamine

derivative, $\underset{SH\cdot C\,\cdot\,S}{\overset{N\cdot N}{\underset{||}{C}}}{>}C\cdot S\cdot NHPh$, and that isomeric change subsequently takes place, the radicle $(C_2S_3N_2H)$ being transferred to the para-position relatively to the amido-group.

II [By E. ZIEGELE.]—*Methyldithiodiazolonethiol*, $NMe{<}\underset{CS\cdot S}{\overset{N=C\cdot SH}{|}}$, forms colourless needles which melt at 69° to a yellow oil. The *methylic* salt separates from dilute alcohol in fine, glistening, flat needles, melts at 88°, and dissolves easily in most solvents; like other organic sulphides, it forms an additive compound with bromine, which crystallises from benzene and melts at 124°. The *benzoyl* derivative melts at 157° and dissolves readily in benzene, chloroform, or absolute alcohol. The *bisulphide* separates from chloroform, on adding alcohol, in glistening, flat, yellowish needles, which soften at 138° and melt at 141°. On oxidation with potassium permanganate, the thiol gives *potassium methyldithiodiazolonesulphonate*, $C_3H_3N_2S_2\cdot SO_3K$, which crystallises in spherical aggregates of slender needles.   T. M. L.

Oxidation of Hydrazoximes. IV. By GIACOMO PONZIO (*Gazzetta*, 1899, **29**, i, 349—357. Compare Abstr., 1898, i, 386, and this vol., i, 717). —*Phenyl-2-methyl-3-ethyl-1 : 2-oxypyrro-1 : 4-diazole*, $O{<}\underset{N\cdot NPh\cdot N}{\overset{CMe-CEt}{|\quad||}}$, obtained by oxidising βa-acetylpropionylhydrazoxime in chloroform solution by means of mercuric oxide, crystallises from light petroleum in faintly yellow, glistening prisms melting at 43—44°, and dissolves in the cold in all ordinary organic solvents except light petroleum, and also to a slight extent in hot water. Its *hydrochloride*, $C_{11}H_{13}N_3O,HCl$, crystallises in white prisms, is decomposed immediately by water with the liberation of the base, and slowly loses hydrogen chloride when left in the air. When the base is reduced in concentrated hydrochloric acid solution by means of granulated zinc, methylethylphenylosotriazole is obtained. The *nitro*-derivative, $C_2ON_3MeEt\cdot NO_2$, prepared by dissolving the phenylmethylethyloxypyrrodiazole in cold concentrated nitric acid, crystallises from alcohol in yellowish plates melting at 131°, and is soluble in benzene, chloroform, or hot alcohol, but dissolves only slightly in ether, light petroleum, or cold alcohol. On reduction in alcoholic solution with zinc and hydrochloric acid, it forms *amidophenylmethylethylosotriazole*, $C_2N_3MeEt\cdot C_6H_4\cdot NH_2$, which melts at 95—96°, and is very soluble in ether, benzene, or chloroform, but almost insoluble in light petroleum.

Phenyl-2-ethyl-3-methyl-1 : 2-oxypyrro-1 : 4-diazole, $O{<}\underset{N\cdot NPh\cdot N}{\overset{CEt-CMe}{|\quad||}}$, prepared from $a\beta$-acetylpropionylhydrazoxime, is a faintly yellow liquid which is heavier than water, does not solidify even at low temperatures, and cannot be distilled unchanged at a low pressure. It is slightly soluble in water, and mixes with all ordinary organic solvents except light petroleum. It is non-volatile in steam. The *hydrochloride*, $C_2ON_3MeEtPh,HCl$, slowly loses hydrogen chloride

when left exposed to the air, and in contact with water is decomposed with liberation of the base. The *nitro*-derivative, $C_2ON_3MeEt \cdot C_6H_4 \cdot NO_2$, crystallises from alcohol in glistening, yellowish plates melting at 156—157°; it is slightly soluble in ether or light petroleum, more so in chloroform or benzene, and when reduced in alcoholic solution by means of zinc and hydrochloric acid yields the amido-compound melting at 95°·

By reducing with zinc and hydrochloric acid the product of the reaction of mercuric oxide on either $\alpha\beta$- or $\beta\alpha$-acetylpropionylhydraz-oxime, methylethylphenylosotriazole, $C_2N_3MeEtPh$, boiling at 282—283° under 751·1 mm. pressure is obtained; von Pechmann (Abstr., 1891, 1110) gives its boiling point as about 270°. Its *nitro*-derivative, $C_2N_3MeEt \cdot C_6H_4 \cdot NO_2$, crystallises from alcohol in long, slightly yellowish needles melting at 127—128°; it is soluble in chloroform, but only slightly so in ether or light petroleum. The *chloro*-derivative, $C_2N_3MeEt \cdot C_6H_4Cl$, crystallises from alcohol in very thin, white needles melting at 81°, is soluble in cold ether, chloroform, or light petroleum, and is volatile in steam; on boiling with nitric acid of sp. gr. 1·52 it is completely converted into nitromethylethyl-phenylosotriazole melting at 127—128°, but with ordinary concentrated nitric acid it yields *chloronitromethylethylphenylosotriazole*, $C_2N_3MeEt \cdot C_6H_3Cl \cdot NO_2$, which crystallises from alcohol in small, faintly yellowish prisms melting at 86—87°, and dissolves only slightly in alcohol or light petroleum, but more readily in ether or benzene. *Bromomethylethylphenylosotriazole*, $C_2N_3MeEt \cdot C_6H_4Br$, crystallises from alcohol in glistening white needles melting at 107—108°, and dissolves in the ordinary organic solvents.   T. H. P.

Metanitroguanazylmethane and Allied Compounds. By EDGAR WEDEKIND [and S. BRONSTEIN] (*Annalen*, 1899, **307**, 293—305). —The *nitrate* of amidoguanidinepyruvic acid, $C_4H_8N_4O_2,HNO_3$, obtained by mixing cold, concentrated, aqueous solutions of amido-guanidine nitrate and pyruvic acid, crystallises in colourless needles containing $\frac{1}{2}H_2O$, which is removed at 120°; the salt melts at 206°. The free *base*, which is trimeric, separates from hot water as a colourless, crystalline powder, dissolving with difficulty in organic media excepting glacial acetic acid; it blackens at about 340° and decomposes at 350—360° without fusion. The *silver* salt, $C_4H_6N_4O_2Ag_2$, detonates when heated, and dissolves in warm ammonia, forming a mirror; the *hydrochloride* crystallises in lustrous leaflets and melts to a red liquid at 245—246°.

Metanitroguanazylmethane, $NO_2 \cdot C_6H_4 \cdot N{:}N \cdot CMe{:}N \cdot NH \cdot C(NH_2){:}NH$, obtained by adding diazotised metanitraniline to an ice-cold solution of amidoguanidinepyruvic acid (compare Wedekind, Abstr., 1897, i, 241), crystallises from alcohol in red needles and prisms melting at 222°; it is insoluble in water and petroleum, but forms deep red solutions in other media. Reduction with stannous chloride and hydrochloric acid changes the red colour to yellow; oxidation with nitric acid gives rise to a *compound* which melts at 180°.

The *compound* $C_9H_{13}N_7O_6$, obtained instead of metanitroguanazyl-

formic acid when diazotised metanitraniline is added to amidoguanidine-glyoxylic acid, crystallises from glacial acetic acid in red needles and melts at 172°.

Acetophenoneamidoguanidine, $CMePh:N\cdot NH\cdot C(NH_2):NH$, prepared by heating acetophenone dissolved in alcohol with aqueous amidoguanidine nitrate and caustic potash, crystallises from dilute alcohol in lustrous, colourless leaflets and melts at 182·5°; it is insoluble in petroleum. M. O. F.

Double Salts of Nicotine Hydrochloride and Cadmium Chloride. By CHARLES GLASER (*J. Soc. Chem. Ind.*, 1899, **18**, 563—564).—When an alcoholic solution of nicotine hydrochloride is added to a large excess of an alcoholic solution of cadmium chloride, the compound $(C_{10}H_{14}N_2,2HCl)_3,7CdCl_2$ is obtained; this crystallises from alcohol in kidney-shaped masses. If, however, the proportions are reversed, a compound, $(C_{10}H_{14}N_2,2HCl)_2,3CdCl_2 + 2H_2O$, is obtained which crystallises from 50 per cent. alcohol in radiate clusters of fine needles and thin plates. In these compounds, the nitrogen was estimated by the soda-lime method, as the Kjeldahl process yielded only about 68 per cent. of the nitrogen as ammonia. L. DE K.

[**Hyoscyamine from**] **Datura Fastuosa.** By W. P. H. VAN DEN DRIESSEN MAREEUW (*Chem. Centr.*, 1899, i, 539; from *Ned. Tijd. Pharm.*, 1899, **11**, 14—19).—The seeds of *Datura fastuosa* contain about 10·9 per cent. of fat and 0·149 of hyoscyamine.

E. W. W.

Constitution of the Alkaloids of the Pomegranate. By ANTONIO PICCININI (*Gazzetta*, 1899, **29**, i, 408—420).—*Dibenzylidenemethylgranatonine*, $C_5NH_8Me\begin{smallmatrix}C(CHPh)\\C(CHPh)\end{smallmatrix}{>}CO$, prepared by the action of hydrogen chloride on a mixture of benzaldehyde and a glacial acetic acid solution of methylgranatonine, crystallises from alcohol in small yellow prisms melting at 200°; it is soluble in benzene or methylic alcohol, and with concentrated sulphuric acid gives an orange-red coloration.

Di-isonitrosomethylgranatonine, $C_5NH_8Me\begin{smallmatrix}C(N\cdot OH)\\C(N\cdot OH)\end{smallmatrix}{>}CO$, obtained by the action of amylic nitrite on methylgranatonine, crystallises from boiling water in sulphur-yellow, acicular prisms, which deflagrate when heated on platinum foil; with a trace of ferrous sulphate in aqueous solution, it gives an intense green coloration, but it has no action on cold ferric chloride. The *hydrochloride*, $C_9H_{13}O_3N_3,HCl$, crystallises from dilute alcohol in yellowish prisms decomposing at 240—250° with evolution of gas; it is slightly soluble in cold, and more so in hot water.

Granatic acid, $COOH\cdot C_5NH_9\cdot CH_2\cdot COOH$, formed when granatoline is oxidised by boiling with a large excess of a sulphuric acid solution of chromic acid, crystallises in colourless prisms, softening at 265°, and melting at 270°. If only a small quantity of the oxidising mixture is employed at a temperature of 50—70°, granatonine is produced.

Granatonine, $C_5NH_9\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}{>}CO$, forms small, colourless crystals

melting at about 128°. It gives a colourless, crystalline *hydrochloride* and a pale yellow, unstable *aurichloride*, which dissolves in boiling water with partial reduction ; the *platinochloride*, $(C_8H_{13}NO)_2,H_2PtCl_6 + 2H_2O$, separates in large, yellow, crystalline leaflets melting, with previous softening, at about 230°, dissolves slightly in cold, and more so in hot water, and loses its water of crystallisation in a desiccator over sulphuric acid. *Nitrosogranatonine*, $NO \cdot C_8H_{12}NO$, separates from a boiling, aqueous solution in colourless leaflets melting at 199°. *Dibenzylidenegranatonine*, $C_{22}H_{21}NO$, separates from alcohol in small, sparkling, yellow crystals melting at 182—183° ; it is readily soluble in benzene or boiling alcohol, slightly so in ether, insoluble in water, and with concentrated sulphuric acid gives an orange-red solution.

By the action of mercuric acetate on granatic acid, a pyridine-carboxylic acid is obtained, and when the product is distilled with barium hydroxide, α-methylpyridine is formed.

The author is of opinion that the characteristic chain of tropinone, $-CH_2 \cdot CO \cdot CH_2-$, is also present in methylgranatonine.   T. H. P.

[Note by Abstractor.—In a paper by Ciamician and Silber (Abstr., 1896, i, 397), a compound termed granatic acid is described ; it is obtained by the oxidation of methylgranatoline, and has the composition $C_9H_{15}NO_4$, whilst the author's granatic acid has the formula $C_8H_{13}NO_4$.   T. H. P.]

Study of an Oxyptomaine. By William Œchsner de Coninck (*Compt. rend.*, 1899, **129**, 109—110).—The following compounds of the oxyptomaine or collidone, $C_8H_{11}NO$ (Abstr., 1898, i, 455), are described. The *platinochloride*, $(C_8H_{11}NO)_2,H_2PtCl_6 + H_2O$, is crystalline, and is completely decomposed by hot, but not by cold, water. The *hydrobromide*, $C_8H_{11}NO,HBr$, is very similar to the hydrochloride, and forms deliquescent, elongated plates, which are easily soluble in cold, but rapidly decomposed by boiling, water. The *aurichloride*, $C_8H_{11}NO,HAuCl_4$, is yellow, and in aqueous solution is decomposed on evaporation on the water-bath. The *mercurichloride*, $(C_8H_{11}NO,HCl)_2,3HgCl_2$, a white precipitate, is insoluble in cold, but slightly soluble in warm, water, and is decomposed on prolonged boiling of its aqueous solution.   H. R. Le S.

Action of Iodine on Bilirubin. By Adolf Jolles (*Monatsh.*, 1899, **20**, 282—306, and *J. pr. Chem.*, 1899, [ii], **59**, 308—319).—The author maintains that, contrary to the view taken by Thudichum (Abstr., 1896, i, 516), the action of iodine in very dilute solution on bilirubin is essentially one of oxidation, and not of substitution, the product being biliverdin.

When bilirubin dissolved in chloroform is treated with a dilute solution of iodine in alcohol, or, better, with Hübl's solution, the same coloured products are obtained as when nitric acid is used as the oxidising agent. The extent of the oxidation depends on the concentration of the solutions, the duration of the action, and the miscibility of the liquids used as solvents. It is also necessary to operate on small quantities at a time, 20—50 milligrams of bilirubin, dissolved in 50—80 c.c. of chloroform, being oxidised with $N/10$ alcoholic solution of iodine, or better, with $N/10$ Hübl's solution. The production of

biliverdin is accomplished by using the materials in the proportions indicated by the equation $C_{16}H_{18}N_2O_3 + 2I + H_2O = C_{16}H_{18}N_2O_4 + 2HI$, the mixture being well shaken and left for some time; the solution of the product is finally washed with very dilute hydrochloric acid until hydriodic acid can no longer be detected in the wash-liquors.

Biliverdin, $C_{16}H_{18}N_2O_4$, is a green, amorphous substance, and resembles the compound obtained by Maly's method (*Annalen*, 1874, **175**, 82) in its solubility in various liquids. The solution in alcohol, rendered slightly acid with mineral acids, gives with acids a bluish-green, and with alkalis a brownish-green, coloration, which gradually fades. On adding ammoniacal alcoholic zinc chloride to the alcoholic solution, a reddish-brown liquid with a green fluorescence is obtained, and when zinc dust is added to the solution of the substance in sulphuric or alcoholic hydrochloric acid, the colour changes to yellowish-green and finally to yellow. When chlorine water is passed down the side of a vessel containing a solution of the substance in alcoholic hydrochloric acid, a blue ring is formed at the bottom of the vessel, the supernatant layer being successively violet, red, and yellow; on adding more chlorine water, the whole becomes yellow, and finally colourless. Potassium permanganate and hydrogen peroxide produce similar colour phenomena.

The spectra given by the author (Abstr., 1894, ii, 466) for bilirubin and biliverdin differ from those of the substances obtained by Maly's method, inasmuch as they exhibit bands due to the presence of an impurity in the substance purchased as pure from a manufacturing firm. Pure biliverdin in alkaline solution shows no absorption bands, but the acidified solution shows a weak band at about D, and one more strongly pronounced between $E\frac{2}{3}F$ and F.

If bilirubin, dissolved in chloroform, is left for some days with excess of Hübl's solution, an amount of the latter equivalent to three atomic proportions of oxygen is used up. The product, for which the author proposes the term *bilixanthin*, may be isolated by washing the chloroform solution with water acidified with hydrochloric acid, the solvent being subsequently removed by careful evaporation. Bilixanthin, $C_{16}H_{18}N_2O_6$, does not exhibit any tendency to crystallise, and is possibly identical with "uroxanthin," a substance obtained by the author from urine. It dissolves in alcohol or chloroform, is soluble for the most part in ether and more so in amylic alcohol, but is insoluble in carbon bisulphide; it is insoluble in the common mineral acids, and the presence of these does not influence its solubility in alcohol; it dissolves for the most part in solutions of alkalis and alkali carbonates. An alcoholic solution of bilixanthin is not altered on addition of hydrochloric acid and zinc dust, or on treatment with hydrogen sulphide, and it does not exhibit any fluorescence with an ammoniacal solution of zinc chloride.

Bilirubin in urine may be fairly accurately estimated by taking advantage of the fact that it is converted into a green colouring matter by means of an alcoholic solution of iodine, two atomic proportions of the latter being required. The method consists in extracting the biliary colouring matters with chloroform, shaking the latter with a known quantity of iodine solution for some minutes, and finally

titrating the excess of halogen with thiosulphate; the description of
the details, however, is lengthy and unsuitable for abstraction.

<div align="right">A. L.</div>

Solvent Power of Pepsin. By JEAN EFFRONT (*Bull. Soc. Chim.*,
1899, [iii], **21**, 683—691).—The solvent power of pepsin, which should
be carefully distinguished from its hydrolytic or peptonising proper-
ties, increases with the acidity of the medium until a maximum is
reached, after which a decrease is observed. Hydrochloric acid is con-
siderably more effective than sulphuric acid, but the amount required
to bring about the best results depends on the state of division of the
proteid, and on other circumstances. The solvent power of different
samples of pepsin may be compared by measuring the time required to
render transparent a definite volume of a 4 per cent. emulsion of albu-
min; a detailed description of this method is given in the paper. The
rate of solution is largely dependent on the temperature, being most
rapid at 65° in the case of neutral solutions, whilst in the presence of
0·15, 0·3, and 0·4 per cent. of hydrochloric acid, the most favourable
temperatures are 65°, 55°, and 50° respectively. In each case, it is found
that solution takes place most rapidly at a temperature approaching
that at which, under the given conditions of acidity, destruction of the
ferment occurs. Peptic solution is retarded by the addition of metallic
salts, and the effect of a number of these was examined quantitatively.
Sulphates, and particularly ammonium sulphate, are most active in this
respect. Caffeine, fatty acids, and alcohols are without influence.

<div align="right">N. L.</div>

Action of Trypsin on the less Complex Chemical Compounds.
By WL. GULEWITSCH (*Zeit. physiol. Chem.*, 1899, **27**, 540—556).—In
view of Kossel's work on the action of trypsin on protamine, and in the
hope that some light might be shed on the constitution of the proteid
molecule, a number of organic compounds such as phenetoil, ethyl-
aniline, diphenylcarbamide, acetanilide, orthacetamidobenzoic acid,
and salol, were subjected to the action of the tryptic ferment. The
results of the experiments were negative, except in the case of para-
diacetylamidophenol, which, with powerful solutions of trypsin, gave
rise to acetic acid. Nencki and Blank have stated (*Arch. exp. Path.
Pharm.*, **20**, 377) that hippuric acid is decomposed by trypsin; this
was not confirmed; possibly the trypsin they used was contaminated
with the fat-splitting ferment of the pancreas. W. D. H.

Diastatic Functions of Indigo-yielding Plants. By L.
BRÉAUDAT (*Compt. rend.*, 1899, **128**, 1478—1480. Compare this vol.,
i, 232).—The indigotic fermentation of the leaves of *Isatis alpina*,
which is brought about by a hydrolytic diastase and an oxydase
present in the leaves, is promoted by the presence of ammonia, baryta,
magnesia, and the carbonates of the alkali or alkaline-earth metals,
either dissolved or in suspension in the fermenting liquor. In presence
of acids or neutral salts, no formation of indigo is detected. The
alkali only affects the action of the oxydase, the feeble oxidising power
of which it increases. T. H. P.

Protamines. By ALBRECHT KOSSEL (*Zeit. physiol. Chem.*, 1899, **26**, 588—592. Compare Abstr., 1896, i, 582; 1898, i, 714).—Renewed experiments have shown that histidine is not formed in the hydrolysis of clupeine, salmine, or scombrine with dilute sulphuric acid. Nor does clupeine yield lysine in these circumstances; a substance, which has the composition of an amidovaleric acid and sublimes when heated cautiously, is obtained, however, along with another more soluble substance. And sturine is now found to yield some substances of a similar nature in addition to the three hexon bases, arginine, histidine, and lysine.

Protamines, therefore, must be subdivided into two groups: those of the one group, exemplified by sturine, yield all three hexon bases when hydrolysed; those of the other, namely, clupeine, salmine, and scombrine, yield arginine only. If a protamine nucleus does form the basis of the albumin molecule, it must be one of the sturine type, since the proteids, like sturine, yield all three hexon bases.

C. F. B.

Preparation and Detection of Lysine. By ALBRECHT KOSSEL (*Zeit. physiol. Chem.*, 1899, **26**, 586—587).—From the products of decomposition of proteids, the bases are precipitated with phosphotungstic acid, the precipitate is decomposed with baryta, from the filtered liquid the histidine and arginine are precipitated with silver sulphate and baryta (Abstr., 1898, i, 715), and the filtrate is evaporated to a syrup and mixed with alcoholic picric acid, when lysine picrate, $C_6H_{14}N_2O_2, C_6H_3N_3O_7$, separates; this is recrystallised from a small quantity of boiling water. To convert it into the hydrochloride, it is dissolved in dilute hydrochloric acid, the picric acid is removed by extraction with ether, and the liquid is then evaporated to a syrup and mixed with a little hot alcohol, when lysine hydrochloride crystallises out as the mixture cools. C. F. B.

Arginine. By WL. GULEWITSCH (*Zeit. physiol. Chem.*, 1899, **27**, 178—215, and 368—369).—Arginine has been prepared from the testicles of salted herrings, and a number of its salts examined. Most of these have been prepared before (Schulze and Steiger, Abstr. 1886, 725; Hedin, Abstr., 1895, i, 160; 1896, i, 193); the hydrochloride however, as crystallised from alcohol, contained $1H_2O$ (Schulze and Steiger describe it as anhydrous; Hedin, with $1H_2O$), and the copper nitrate compound, $3\frac{1}{2}H_2O$ ($3H_2O$, according to these authors). A crystalline *phosphotungstate*, $3C_6H_{14}N_4O_2, 2H_3PO_4, 24WO_3 + 10H_2O$, and a *mercurichloride* compound, melting and decomposing at 186—189° are described, apparently for the first time: in the latter, the ratio Hg : Cl is 1 : 1, and hence the compound is of the nature of a mercuric derivative of the base. The hydrochloride melts and decomposes at about 209° when anhydrous, the nitrate melts partially and begins to decompose at 175°; the acid nitrate (with $2HNO_3$) melts and decomposes at 144·5—145°; the copper nitrate compound melts at 112—114°, or at 232—234° with decomposition when anhydrous; the copper sulphate compound melts at about 110°, and when anhydrous decomposes at 235—238°; the silver nitrate compound

(with $AgNO_3$) decomposes at 164°, the acid compound (with $HNO_3,AgNO_3$) melts and decomposes at about 180°. The specific rotation, $[\alpha]_D$, calculated for the arginine, is about 12·5° for the hydrochloride in aqueous solution, and is raised to about 25·5° by addition of excess of hydrochloric acid, and lowered to about 11·5° by addition of a slight excess of barium hydroxide; for the nitrate, the value is about 12·5°, raised to about 25·5° by the addition of excess of acid (about 13° for the compound with $HNO_3,AgNO_3$); for the sulphate 10·5°, raised to 22·5°. A *silver* derivative of arginine (compare Kossel, Abstr., 1898, i, 715) was precipitated by adding silver nitrate to a solution of one of the silver nitrate compounds, until the ratio $AgNO_3 : C_6H_{14}N_4O_2$ was 2 : 1, and then adding just enough alkali to combine with all the nitric acid present; the resulting compound is amorphous and unstable in daylight; it appears to consist mainly of $C_6H_{12}N_4O_2Ag_2 + H_2O$ mixed with a little $C_6H_{11}N_4O_2Ag_3 + H_2O$.

The arginine itself was prepared by boiling the testicles with dilute sulphuric acid (1 : 2) for 8 hours, neutralising with chalk, adding silver nitrate to the concentrated filtrate until a drop gave a brownish precipitate with baryta water, saturating the filtered liquid with baryta water, washing the precipitate of arginine-silver with water, decomposing it with hydrogen sulphide, removing carbonic acid with baryta water, neutralising with nitric acid and adding silver nitrate and ammonia alternately so long as a small quantity of either produced a further precipitate, filtering from the precipitated silver compounds of histidine and thymine, neutralising with nitric acid and evaporating to the crystallising point, purifying the crystals of the silver compound (with $HNO_3,AgNO_3$) by recrystallisation from hot water, converting these into arginine-silver, decomposing this with hydrogen sulphide, and evaporating the filtrate to the crystallising point. Arginine decomposes at 207—207·5°, and has the properties of an alkali; for instance, it absorbs carbonic anhydride from the air. Its molecular weight determined by cryoscopic methods, using water as solvent, agrees with that required by the formula $C_6H_{14}N_4O_2$. The *dibenzoyl* derivative, $C_6H_{12}N_4O_2Bz_2$, forms needles or tablets belonging to the rhombic system, melts at 217·5—218°, and in its properties shows much resemblance to ornithuric acid.

The discrepancy between the author's polarimetric results and those of Schulze and Steiger is due to the fact that these observers stated the rotation of an aqueous solution of arginine nitrate (of vegetable origin) in degrees of the Ventzke scale, not in angular degrees. This being so, the rotation proves to be practically identical with that of arginine from animal sources, and there is no reason therefore to suspect the existence of two dextrorotatory arginines.   C. F. B.

Thymine. By WL. GULEWITSCH (*Zeit. physiol. Chem.*, 1899, **27**, 292—296).—Thymine, obtained by boiling herrings' testicles with dilute sulphuric acid (preceding abstract), was compared, as regards crystalline form, with that from the thymus and from the milt of the sturgeon (Kossel, Abstr., 1894, i, 156, 631; 1896, ii, 537). The crystals sometimes have a rounded outline, but frequently are bounded by straight lines meeting at 90° or 45°; they show extinction parallel

to one set of these lines. Some characteristic shapes are figured in the paper. C. F. B.

Chemical Examination of Laben. By NICOLAS GEORGIADÈS (*J. Pharm.*, 1899, [vi], 9, 519—521).—Laben is produced by the action of a special ferment on the milk of the cow or goat, and is used as a food by the people of Syria. After the introduction of the ferment, the milk coagulates and the lactose is decomposed into carbonic, acetic, and lactic acids, the last two increase in amount until the third day after the introduction of the ferment, when butyric fermentation sets in and the liquid is no longer fit for food. Small quantities of alcohol and glycerol were also found in the liquid. The butyric fermentation is accidental and does not occur, if, after the ferment is introduced, the milk is put into flasks which have been carefully cleaned. H. R. LE S.

Action of Pepsin and Pancreatic Juice on Albumin. By V. HARLAY (*J. Pharm.*, 1899, [vi], 9, 424—428. Compare this vol., i, 656).—The results confirm the author's statement (*loc. cit.*), that the absence of a turbidity, on the addition of nitric acid to the filtrate from the products of digestion, is no proof that the digestive action is ended. The digestive action of pepsin and pancreatic juice on albumin is quite analogous to that on fibrin, except that pancreatic juice acts much more slowly on the former, and digestion is not complete even after the addition of sodium hydrogen carbonate. The juice of *Russula delica* gave a colour change of red to green with the liquid from the pepsin digestion, and of red to black with that from pancreatic digestion. Tyrosine was found in the liquid from the action of the pancreatic juice on albumin. H. R. LE S.

Two New Reactions of the Products of the Digestive Action of Pepsin and Pancreatic Juice. By V. HARLAY (*J. Pharm.*, 1899, [vi], 9, 468—470. Compare preceding abstract).—The green colour produced by the action of the juice of *Russula delica* on the products of the digestive action of pepsin on albumin or fibrin, is changed to a bright red by the addition of a few drops of an alkali, but is restored when acid is afterwards added. On similar treatment, the dark brown liquid resulting from the digestive action of pancreatic juice does not show a colour change.

With liquids resulting from a pancreatic digestion of albumin or fibrin, bromine water produces a precipitate which redissolves when shaken, giving rise to a red liquid, changing to a reddish-purple on further addition of bromine, a brownish-purple precipitate being finally formed. With liquids resulting from the digestive action of pepsin, only a slight turbidity and a faint, dirty violet coloration are produced, a yellowish precipitate being formed on the addition of excess of bromine. H. R. LE S.

Solubility of Proteoses and Peptones in Alcohol. By JEAN EFFRONT (*Bull. Soc. Chim.*, 1899, [iii], 21, 676—680).—The use of alcohol for the separation of the products of peptic digestion has been proposed by several experimenters, but little is definitely known regarding the actual solubility of the substances concerned. The

relative proportion of soluble and insoluble matter yielded by different specimens of commercial peptone varies greatly, according to the amounts of alcohol and peptone employed, and this result appears to be due not so much to real differences between the products examined as to their acidity. Experiment shows that the precipitate formed by adding alcohol to peptone solutions decreases rapidly as the amount of acid present increases, until finally no precipitate is obtained. It is only by working with neutral solutions that concordant results can be obtained.   N. L.

Histones. By IVAR BANG (*Zeit. Physiol. Chem.*, 1899, **27**, 463—486). —The term histone has been applied to various proteids; it was first used by Kossel for a proteid extracted from nucleated red blood corpuscles with hydrochloric acid. Next Lilienfeld separated from the thymus, spleen, and testis a histone combined with nuclein (nucleohistone); then Mathews regarded the substance arbacin, which he prepared from the sea-urchin, *Arbacia*, as a histone, and, lastly, Schulz regards globin, the proteid constituent of hæmoglobin, as belonging to the same category. These four substances differ from each other very considerably in elementary composition, and the present inquiry was to determine whether the histones should be regarded as a separate, well characterised group of proteids. The substances examined were the four just mentioned, except that, in place of arbacin, the similar substance scombrine, prepared from mackerel sperm, was used. It is admitted that the histones give no single distinctive reaction, but from the fact that all give a certain number of reactions, the group is considered to be sufficiently well defined. These reactions are the following: (1) They are precipitated by ammonia, and the precipitate is insoluble in excess of that reagent in the presence of ammonium salts; (2) they are precipitated by nitric acid; the precipitate dissolves on heating, and reappears on cooling; (3) they are precipitated by boiling in a neutral solution, except when the solution contains little or no salt; (4) neutral solutions are precipitated by alkaloidal reagents, and (5) they precipitate albumin from its solutions.   W. D. H.

Definite Compounds of Proteids [with Mineral Acids]. By THOMAS BURR OSBORNE (*J. Amer. Chem. Soc.*, 1899, **21**, 486—493).— The author finds that the proteids hitherto prepared are definite compounds of protein with mineral acids, or mixtures of such compounds. All these substances are acid to phenolphthalein, slightly acid or neutral to litmus, and alkaline to lacmoid or tropæolin; by means of the last two indicators, it is found that proteids are capable of combining with further quantities of acid.

In the case of edestin, the nature of the combined acids depends on the method of preparation; thus, when precipitated from sodium chloride solution, it contains mostly hydrochloric acid, and when thrown down from ammonium sulphate solution, it is united to sulphuric acid. When either product is suspended in water and made neutral to phenolphthalein by dilute caustic potash, the alkali unites with the acid from the edestin and the proteid is precipitated in the free state. Thus obtained, edestin is insoluble in water, but dissolves readily in decinormal acid or alkali. It is soluble also in 10 per cent. aqueous

sodium chloride; the solution is neutral to phenolphthalein, but alkaline to litmus and lacmoid, and when heated on a water-bath is slowly and imperfectly coagulated. From this brine solution, the edestin is slightly precipitated by saturating with salt, more so by saturating with magnesium sulphate, and completely on saturating with sodium sulphate at 34°. On dialysing the liquid obtained by gradually mixing a 10 per cent. sodium chloride solution of edestin with an equal volume of the same salt solution containing 1 c.c. of decinormal hydrochloric acid per gram of edestin, a crystalline deposit is obtained, of which the part insoluble in water consists of *edestin monohydrochloride*; it separates from a diluted brine solution in octahedral crystals. On treating edestin with insufficient hydrochloric acid to completely dissolve it, the part dissolved consists of a *dihydrochloride* which is soluble in water, but is reprecipitated by the addition of very small quantities of alkali salts. It dissolves in 10 per cent. sodium chloride solution, giving a liquid from which, on dialysis, it separates in octahedra; it crystallises well from a diluted brine solution, and in either aqueous or salt solutions is acid to phenolphthalein or litmus, but alkaline to lacmoid. Sodium chloride solutions of both derivatives give a flocculent precipitate when heated at 99°, and, on saturation with sodium chloride, magnesium sulphate, or sodium sulphate, behave similarly to edestin.   T. H. P.

Egg-Albumin. By THOMAS BURR OSBORNE (*J. Amer. Chem. Soc.*, 1899, **21**, 477—485).—In the preparation of crystallised albumin, the author finds that instead of adding acetic acid to the semi-saturated ammonium sulphate solution of egg-albumin, as recommended by Hopkins and Pinkus (Abstr., 1898, i, 456), the addition of hydrochloric acid, equivalent in quantity to the acetic acid, gives a quicker precipitation of the substance. The products thus obtained, which are acid to litmus or phenolphthalein, but alkaline to lacmoid or tropæolin, are regarded as compounds of albumin with acids. Of the first crop of crystals deposited, 1 gram required for neutralisation to litmus 2·05 c.c. of $N/10$ KOH, and to phenolphthalein 1·30 c.c., the difference being 0·75 c.c. The mean difference for all the crystals obtained both by means of acetic and hydrochloric acids was 0·71 c.c. If the number 15,000, as given by Sabanéeff (Abstr., 1890, 1215), for the molecular weight of albumin is correct, and the acid and albumin unite in molecular proportion, then 1 gram of albumin would require 0·67 c.c. of the alkali; also, if 3 mols. of acid combine with 1 mol. of albumin, then 1 gram of albumin would require for its neutralisation 2 c.c. of $N/10$ alkali. The acid with which the albumin is united is almost entirely, if not altogether, organic, but its nature is unknown.

The coagulation of albumin is greatly influenced by the amount of acid present; exact neutralisation to phenolphthalein prevents coagulation, which, however, readily takes place on the water-bath in the presence of 3 mols. of acid to 1 of albumin.

Pure albumin gives in aqueous solution a mean specific rotation $[a]_D - 28° 42'$; in decinormal acid or alkali solution, the rotation increases slightly with the amount of alkali or acid present. Several analyses are quoted in the paper.   T. H. P.

Crystallisation of Blood-Albumin. By S. GRUZEWSKA (*Compt. rend.*, 1899, **128**, 1535—1537).—The author has succeeded in crystallising blood-albumin from the guinea-pig, cat, ox, and adder. The blood is collected in a 0·2 per cent. solution of sodium oxalate and centrifugated, the cold residue being mixed with a saturated solution of ammonium sulphate to eliminate the globulines, which are filtered off. The filtered liquor is then kept cool by a freezing mixture for a time varying with the nature of the serum (22 hours at $-1°$ in the case of guinea-pig's blood), and when left at the ordinary temperature crystals of albumin are obtained. The serum of the guinea-pig yields five different forms of crystals, some apparently belonging to the hexagonal system.   T. H. P.

Crystalline Forms of Albumin. By ARTHUR WICHMANN (*Zeit. physiol. Chem.*, 1899, **27**, 575—593).—The author has investigated the crystalline forms of egg-albumin, serum-albumin, and lactalbumin, and concludes that they are probably identical, or at least isomorphous; thus, on adding ammonium sulphate to an aqueous solution of a mixture of egg- and serum-albumin or of all three albumins, only one crystalline modification can be obtained. It seems probable also, from their optical behaviour, that the four different crystalline modifications of serum-albumin described by Michel and Gürber belong to the hexagonal-pyramidal class of the hexagonal system, and are all derived from the same fundamental form. The crystals of serum-albumin are as a rule larger and better defined than those of either egg-albumin or lactalbumin; all three forms, however, closely resemble one another in completely absorbing the colouring matter from dilute dye solutions, becoming coloured in the process although otherwise remaining unchanged. It is noteworthy, however, that when the coloured crystals are dried they become amorphous throughout their substance, without losing their crystalline shape, whilst the undyed crystals, under similar treatment, fall to pieces in becoming amorphous. Mineral salts such as gold chloride, silver nitrate, and cadmium borotungstate are also readily absorbed by crystalline albumin; potassium permanganate, which readily acts on aqueous albumin, forming a gelatinous substance and a brown precipitate, is apparently without action on albumin crystals, beyond tinting them yellowish-brown and rendering their material amorphous without changing their shape.

The crystalline compound of ammonium sulphate with albumin, containing about 5 per cent. of the latter, described by Harnack (Abstr., 1891, 476), is shown to consist merely of crystals of ammonium sulphate containing inclusions of aqueous albumin.

When crystals of egg albumin (double refraction positive) are left in contact with the mother liquor, coagulation occurs and the mass becomes isotropic; after some time, however, crystals separate having negative double refraction which differ therefore from the original form. On warming, the amorphous variety is regenerated, but this, when left, undergoes transformation into the negatively refracting modification. The crystalline, soluble variety, which also exists in an amorphous form and appears to be monotropic, is termed *a-albumin*,

and the name *β-albumin* is given to the insoluble, amorphous form, which becomes negatively double-refracting and is enantiotropic.

W. A. D.

Composition and Hydrolysis of the Albumin of the Carob Seed (Ceratonia Siliqua). By Émile Bourquelot and Henri Hérissey (*Compt. rend.*, 1899, **129**, 228—231).—When the albumin of the grain of *Ceratonia siliqua* is heated with dilute sulphuric acid (4 : 100) at 110°, it yields a mixture of mannose (compare Alberda van Ekenstein, Abstr., 1898, i, 118) and galactose, both of which the author has isolated in a crystalline form and identified by various physical properties and chemical reactions. The quantities obtained are considerable and no other sugar seems to be formed. The nature of the insoluble portion, amounting to about 1/7 of the albumin employed, is under investigation.

C. H. B.

Molecular Weight of Proteids. By Wilhelm Vaubel (*J. pr. Chem.*, 1899, **60**, 55—71).—A review of the methods by which the molecular weight of proteids can be determined : These comprise (1) the freezing point or boiling point of a dilute solution; (2) the analysis of proteid salts, especially metallic compounds; (3) the determination of the total percentage of sulphur, and the percentage which will act on alkaline lead solutions; (4) the estimation of the proportion of halogen, &c., in substituted proteids; (5) the estimation of the quantity of the various products of hydrolysis, especially tyrosine, aspartic acid, and arginine. A summary is given of the most reliable of the results obtained by these methods with oxyhæmoglobin, globin (from hæmoglobin), crystallised serum-albumin, conglutin, egg-albumin, and casein. The author concludes that, in the case of the albumins, the data are sufficient to give a satisfactory estimate of the molecular weight, but that further information must be obtained with regard to the albumoses and peptones. T. M. L.

Properties of Nucleo-Proteids. By Filippo Bottazzi (*Real. Accad. dei Linc.*, 1899, **8**, 505—513).—The nucleo-proteids examined were extracted from very fresh animal organs in such a way as to remove all enzymes, the proteid and biliary substances, and the hæmoglobin. The experiments were made in Wolff bottles so arranged that no putrefying action took place.

Towards sodium carbonate solution, nucleo-proteids show an acid behaviour, the alkalinity of the solution being gradually destroyed.

On adding to a solution of splenic or hepatic proteid sufficient oxyhæmoglobin solution to cause the liquid to show distinctly the two absorption striæ in the spectroscope and allowing to remain, it is found that, after 3 to 5 hours, all traces of the oxyhæmoglobin have disappeared ; if an excess of the latter is added so that the absorption striæ unite to form a wide band, the latter gradually becomes separated into two distinct parts, which finally disappear. After this, the liquid assumes a dirty, brownish colour, but at no period of the action can the spectrum of hæmoglobin, or of methæmoglobin, be detected. Although no important differences between the actions of splenic and hepatic proteids were observed, in all these experiments the nucleo-

proteid from ox liver showed itself to be the most active. The only substance exerting a decomposing action on oxyhæmoglobin similar to that attributed to the nucleo-proteid is sodium carbonate, and this is found to have a very much slower action.

When glycogen is dissolved in solutions of hepatic proteid under conditions which do not allow of the presence of an enzyme, the glycogen disappears; the best temperature is 38—40°, and it is not necessary for the liquid to be aërated.   T. H. P.

Cellular Membrane of Gentian Root. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1899, [vi], 9, 330—331. Compare Abstr., 1898, i, 607, and 1899, i, 93).—Twenty-five grams of powdered gentian root which had been previously treated with cold water, boiling alcohol, and dilute sulphuric acid, were treated with a mixture of 125 grams of sulphuric acid and 42 grams of water, and left at the ordinary temperature for 24 hours; the volume was then made up to 1000 c.c., and the filtrate, after further dilution to 5000 c.c., was boiled for 6 hours. The sulphuric acid was removed by means of chalk, the liquid evaporated, and the residue recrystallised from boiling absolute alcohol, when a crystalline sugar was obtained which gave $[a]_D + 52 \cdot 51$, and from its melting point (143—144°), and that of its osazone (205°), is identified as dextrose.   H. R. LE S.

Decomposing Action of Water on Hæmatins. By PAUL CAZENEUVE and P. BRETEAU (*Bull. Soc. Chim.*, 1899, [iii], 21, 427—428).—After being subjected to the action of boiling water and then dried at 135°, hæmatin is insoluble in cold dilute ammonia solution. Hæmatins from the blood of oxen, horses, and sheep, after being washed with boiling water on the filter for an hour or so, all showed diminished percentages of carbon, oxygen, nitrogen, and iron. The action of the hot water is thus one of oxidation.   T. H. P.

Organic Chemistry.

Italian Petroleums. By ETTORE CECCHI-MENGARINI (*Gazzetta*, 1899, **29**, i, 460—470).—Petroleums from Salsomaggiore and Ozzano in the province of Parma, and from Valleia near Piacenza, have been examined. The portion distilling between 150° and 270°, which is that used for illuminating purposes, was separated into fractions with boiling points covering a space of 10°. The density of each fraction and its solubility in a mixture of equal volumes of chloroform and 93 per cent. alcohol were measured. The densities of the different fractions show very close agreement with the corresponding values for Russian petroleum, but differ greatly from those of American petroleum ; the same is the case with the curves connecting the density with the solubility in the alcohol–chloroform mixture. The author concludes that Italian petroleum consists of hydrocarbons of the naphthene series.   T. H. P.

Hydration of Acetylene. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1899, [vii], **17**, 297—302).—An account of work already published (this vol., i, 264 and 397).   G. T. M.

Silver Derivatives of Acetylene. By MARCELLIN P. E. BERTHELOT and MARCEL DELÉPINE (*Compt. rend.*, 1899, **129**, 361—378). —The formation of disilver-acetylene by the action of acetylene on ammoniacal silver nitrate develops $+ 15·55$ Cal., and hence $C_2 + Ag_2 = C_2Ag_2$ pptd. develops $- 87·15$ Cal. When dried in air at the ordinary temperature, the precipitate contains 89·6 per cent. of silver, which agrees with the formula C_2Ag_2, and hence it is neither an oxide nor a hydroxide. The action of acetylene on silver oxide would develop $+ 22·25$ (H_2O gas) or $+ 32·95$ Cal. (H_2O sol.). When heated in a vacuum, disilver-acetylene detonates with a strident noise and a reddish flame, carbon being deposited on all parts of the tube. The production of flame is due to the high temperature (about 4000°) of the decomposition causing volatilisation of the carbon, the condensation of which, in its turn, develops a large quantity of heat. The compound is decomposed by gaseous hydrogen chloride and dilute hydrochloric acid, with liberation of acetylene and development of $+ 43·25$ Cal. and $+ 8·4$ Cal. respectively, but is not attacked by dilute sulphuric or nitric acid, because such reactions would be markedly endothermic. Gaseous nitric acid, however, oxidises it violently.
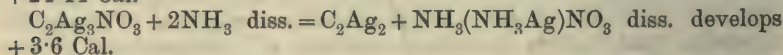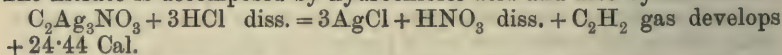
The direct formation of disilver-acetylene would absorb a much larger quantity of heat than the formation of acetylene itself. Chemical analogies indicate the possible existence of a compound C_2HAg, but thermochemical analogies indicate that it would be extremely unstable. The substitution of sodium for hydrogen in gaseous hydracids and in acetylene is always exothermic, whereas in the case of silver the reaction is endothermic with hydrogen fluoride, hydrogen cyanide, and nitric acid, and especially so with acetylene ($- 29·05$ Cal.). Disilver-acetylene is not, however, decomposed by

water, because the action of acetylene on the silver oxide that would be found is markedly exothermic : C_2H_2 gas $+ Ag_2O + xH_2O = C_2Ag_2 + (H_2O)_{x+1}$ develops $+ 32\cdot95$ Cal.

The action of acetylene on solutions of silver salts yields compounds of the general type C_2Ag_2, AgR, which the author regards as salts of a special radicle, C_2Ag_3, the general type then being C_2Ag_3R. The reaction C_2H_2 gas $+ 3AgNO_3$ diss. $= C_2Ag_3NO_3$ pptd. $+ 2HNO_3$ diss. develops $+ 32\cdot4$ Cal., or, if the acetylene is dissolved, $+ 27\cdot1$ Cal., which gives $+ 5\cdot3$ Cal. for the heat of dissolution of acetylene, and this agrees with Villard's determination.
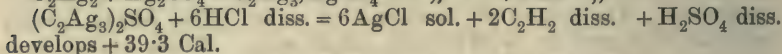
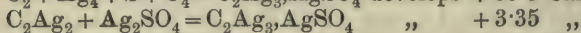$C_2 + Ag_3 + N + O_3 \quad = C_2Ag_3NO_3 \quad$ develops $- 54\cdot3$ Cal.
$C_2Ag_2 + AgNO_3$ sol. $= C_2Ag_3NO_3 \qquad ,, \qquad + 4\cdot15 \quad ,,$
$C_2Ag_2 + AgNO_3$ diss. $= C_2Ag_3NO_3$ pptd. $,, \qquad + 9\cdot85 \quad ,,$
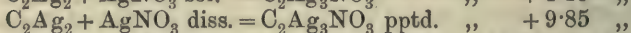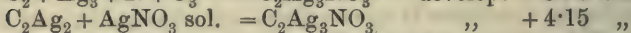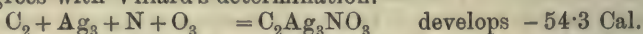
The nitrate is decomposed by hydrochloric acid and also by ammonia.

$C_2Ag_3NO_3 + 3HCl$ diss. $= 3AgCl + HNO_3$ diss. $+ C_2H_2$ gas develops $+ 24\cdot44$ Cal.

$C_2Ag_3NO_3 + 2NH_3$ diss. $= C_2Ag_2 + NH_3(NH_3Ag)NO_3$ diss. develops $+ 3\cdot6$ Cal.

The nitrate is oxidised by strong nitric acid with liberation of nitrogen oxides and formation of some silver cyanide.

The action of acetylene on silver sulphate solution yields the compound $C_2Ag_3, AgSO_4$ when the silver salt is in excess, and the compound $(C_2Ag_3)_2SO_4 + C_2Ag_3, AgSO_4$ when the action of the gas is continued. The latter salt is insoluble, and hence the final compound, $(C_2Ag_3)_2SO_4$, described by Plimpton, is only formed when the precipitate remains for a long time in contact with the acetylene solution.

C_2H_2 diss. $+ 2AgSO_4$ diss. $= C_2Ag_3, AgSO_4$ pptd. $+ H_2SO_4$ diss. develops $+ 21\cdot2$ Cal.

$C_2 + Ag_4 + S + O_4 = C_2Ag_3, AgSO_4$ develops $+ 83\cdot3$ Cal.
$C_2Ag_2 + Ag_2SO_4 = C_2Ag_3, AgSO_4 \qquad ,, \qquad + 3\cdot35 \quad ,,$
$(C_2Ag_3)_2SO_4 + 6HCl$ diss. $= 6AgCl$ sol. $+ 2C_2H_2$ diss. $+ H_2SO_4$ diss. develops $+ 39\cdot3$ Cal.

$S + O_4 + C_6 + Ag_6 = (C_2Ag_3)_2SO_4$ develops $+ 2\cdot8$ Cal.
$Ag_2SO_4 + 2C_2Ag_2 = (C_2Ag_3)_2SO_4 \qquad ,, \qquad + 10 \quad ,,$
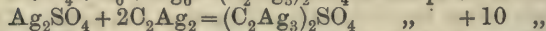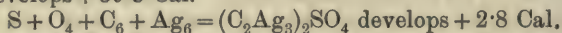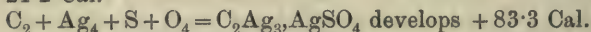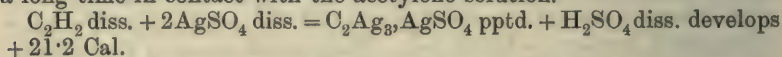
The difference between the heats of formation of the nitrate, $C_2Ag_3NO_3$, and the sulphate, $(C_2Ag_3)_2SO_4$, is practically identical with the difference between the heats of formation of silver nitrate and silver sulphate.

Silver chloride dissolved in ammonia yields three products, according to the relative proportions of silver salt and acetylene and the time of action, namely, C_2Ag_3Cl, C_2Ag_3Cl, C_2Ag_2, or $C_2Ag_2(C_2Ag_3)Cl$, and $C_2Ag_3Cl, 2C_2Ag_2$, the first being yellowish, the second lemon-yellow, and the third deep yellow. The decomposition of the first by hydrochloric acid develops $+ 11\cdot8$ Cal., and of the second $+ 23\cdot3$ Cal., whilst the heats of formation from the elements are $- 56\cdot4$ Cal. and $- 141\cdot5$ Cal. respectively. The combination of silver chloride with 1 mol. of disilver-acetylene develops $+ 1\cdot75$ Cal., and with 2 mols. $+ 3\cdot8$ Cal. It is noteworthy that the heats of formation of the compounds C_2Ag_3Cl and $C_2Ag_3NO_3$ are practically identical, like the heats of formation of silver nitrate and chloride.

Silver iodide dissolved in potassium iodide solution containing a

small quantity of potassium hydroxide, which is renewed from time to time as the action of the acetylene is continued, yields the compound C_2Ag_3I,AgI, which is decomposed by hydrochloric acid with development of $+12.65$ Cal.; its heat of formation from its elements is -57.85 Cal., and from $C_2Ag_2 + 2AgI$, $+0.90$ Cal. The compound C_2Ag_3I is obtained by the carefully regulated action of potassium iodide on the corresponding nitrate; it is decomposed by hydrochloric acid with development of $+13.85$ Cal., and its heat of formation from its elements is -73.2 Cal. When heated, the sulphate, chloride, and iodide detonate somewhat feebly, and the nitrate violently.

The authors regard the metallic derivatives of acetylene as analogous to the nitrides derived from ammonia, and the compound C_2Ag_3 as analogous to ammonium NH_4. C. H. B.

Action of Acetylene on Copper. By HANS ALEXANDER (*Ber.*, 1899, **32**, 2381—2384. Compare this vol., Erdmann and Köthner, i, 21; Sabatier and Senderens, i, 555).—When pure dry acetylene is passed over spongy copper contained in a tube heated at 240—250°, the metal appears to swell enormously and finally forms a uniform, cork-like mass; when the amount of copper in the product has fallen to 2 per cent., further action ceases.

The product, when freed from liquid hydrocarbons by warmth or exposure to air, is odourless. It decomposes and becomes luminous when strongly heated in air, giving off vapours having a peaty odour. By treatment with hydrochloric acid containing ferric chloride, it loses the whole of its copper, but afterwards contains about 0.2 per cent. of iron; the substance in this case is somewhat lighter in colour, but otherwise is similar in appearance to the specimens containing copper. Analysis of the material gave an amount of carbon equal to 88—89 per cent.

The gas which passes out from the tube during the above experiment is completely absorbed by ammoniacal cuprous chloride, yielding the characteristic copper acetylide.

The formula $C_{44}H_{64}Cu_3$ has been ascribed by Erdmann and Köthner (*loc. cit.*) to a product obtained by heating copper in acetylene at 230°, and they supposed it to be a copper–acetylene compound. The author, having repeated the experiment of these workers, concludes that the copper in their product was retained mechanically.

It is believed that the influence of the copper partakes of the nature of a contact phenomenon, and that the action consists in the polymerisation of the acetylene, and results also in the formation of naphthene-like hydrocarbons; the hydrogen liberated in the production of these substances is not set free, but would seem to be absorbed either by the resulting hydrocarbon or by the cork-like material.

A. L.

Boiling Points of Compounds of the General Formula $CH_3 \cdot (CH_2)_n \cdot R$. By ENRICO BOGGIO-LERA (*Gazzetta*, 1899, **29**, i, 441—459).—The absolute boiling points of the normal compounds of homologous series of the general formula $CH_3 \cdot (CH_2)_n \cdot R$ are equal to the square roots of numbers in arithmetical progression; this relation is expressed by the formula $T = k\sqrt{M+c}$, where T is the boiling point

on the absolute scale, M the molecular weight, and k and c constants whose values are in general different for different homologous series. For the value $n = 0$ in the general formula, that is, for the first member of each series, the relation does not hold good. Tables are given showing the experimental and calculated numbers for the normal monochloro-, monobromo-, and moniodo-paraffins, amines, nitro-paraffins, ketones, alkylic formates, acetates, propionates, butyrates, valerates, hexoates, heptoates and octoates, and for alkyl-ethyl, alkyl-propyl, alkyl-butyl, alkyl-heptyl, alkyl-phenyl, alkyl-orthotolyl, alkyl-paratolyl, and alkyl-metatolyl ethers. The agreement for all these series is good, the greatest divergences being with the amines, nitro-derivatives, and ketones, where the differences between the calculated and observed temperatures are sometimes as much as 3 or 4°. For the alkylic chlorides, bromides, and iodides, the formulæ are respectively $T = 38\cdot66 \sqrt{M - 10}$, $T = 38\cdot98 \sqrt{M - 45}$, and $T = 39\cdot1 \sqrt{M - 78}$; it is noticeable that the three values of c, namely, -10, -45, and -78, stand very nearly in arithmetical progression.

<div align="right">T. H. P.</div>

Action of Nitric Acid on Saturated Hydrocarbons. VI. Nitration in Sealed Tubes and in Open Vessels. Separation of Mono- from Dinitro-compounds. By MICHAËL I. KONOWALOFF (*Chem. Centr.*, 1899, i, 1063—1064; from *J. Russ. Chem. Soc.*, 1899, **31**, 57—69).—When hydrocarbons are heated with nitric acid in closed tubes, the yield of nitro-compounds obtained is dependent on the sp. gr. of the acid and the temperature at which the mixture is heated. The acid usually employed has a sp. gr. $1\cdot075$—$1\cdot2$, and the temperature varies from 100—130°. Ethylbenzene and diphenyl-methane, which are easily nitrated by heating in tubes at 100°, are also readily attacked in open vessels by acid of sp. gr. $1\cdot075$, and both these methods yield the same products in the case of heptane, octane, or di-isobutyl. The normal hydrocarbons form mainly secondary nitro-compounds, and the iso-hydrocarbons containing the CH-group yield tertiary nitro-compounds; small quantities of primary nitro-compounds are also produced. Dinitro-compounds are also formed under the same conditions as mononitro-compounds, the yields being increased, however, by employing stronger acid, raising the temperature, and heating the mixture for a longer time. The dinitro-compounds may also be prepared by the action of nitric acid on the mono-nitro-compounds. These two classes of compounds may be separated by (1) fractionally distilling, a vacuum being used in the final distillation, (2) distilling off the mononitro-compounds in steam, or (3) by means of organic solvents. Dinitro-octane, which boils at 170—190° under 16 mm. pressure, may be separated from the mononitro-compound by the first method.

<div align="right">E. W. W.</div>

Electrolytic Reduction of Aliphatic Nitro-derivatives. By PAUL PIERRON (*Bull. Soc. Chim.*, 1899, [iii], **21**, 780—785).—The nitro-derivative is dissolved in a mixture of ethylic alcohol and dilute sulphuric acid, and submitted to electrolysis in contact with a nickel cathode, the liquid being separated from the platinum anode by a porous pot containing dilute sulphuric acid. A cathodic current

density of 0·4—0·75 ampère per square decimetre is employed. If the operation is carried out at a temperature not exceeding 15—20°, the corresponding β-alkylhydroxylamine is produced to the extent of 65—80 per cent. of the theoretical quantity, whilst at 70° further reduction occurs, and a scarcely inferior yield of the amine is obtained. When concentrated hydrochloric or sulphuric acid is employed, small quantities of aldehyde and hydroxylamine, besides other products, are obtained in place of the alkylhydroxylamine; the study of this reaction is being continued. Full details are given in the paper of the application of the methods described to nitromethane, nitroethane, and nitropropane. N. L.

Action of Nitric Anhydride and Peroxide on Olefines. By NICOLAUS I. DEMJANOFF (*Chem. Centr.*, 1899, i, 1064; from *Ann. Inst. Agron. Moscow*, 4, 155—217).—Ethylene nitrosite, C_2H_4,N_2O_3, prepared by passing nitric peroxide and ethylene through ether, separates in lustrous, pseudomonoclinic needles, melts and decomposes at 116—117°, is very slightly soluble in organic solvents, insoluble in water, and when reduced with tin and hydrochloric acid forms ethylenediamine. By the action of nitric anhydride on ethylene at a low temperature, *ethylenic nitrate* is formed; it boils at 114—116° and explodes on distillation. Since the crude product, when reduced, yields acetaldehyde, ethylenediamine, and β-aminoethylic alcohol, it is assumed to be the *compound* $NO_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot NO_2$. *Amylenenitrosate*, $NO_2 \cdot O \cdot CMe_2 \cdot CMe\!:\!NOH$, obtained by the action of nitric anhydride on trimethylethylene, melts at 97°. Analyses of the platinum salts prepared from the mother liquor indicated the presence of the compounds $OH \cdot C_5H_{10} \cdot NH_2$ (?) and $(OH \cdot C_5H_{10})_2NH$ (?). By the action of nitric anhydride on tetramethylethylene, the compounds $C_6H_{12}O_4N_2$, $C_6H_{12}O_5N_2$, and $C_6H_{12}O_6N_2$ are formed, according to the conditions of the experiment, whilst by the action of nitric peroxide only the two former compounds are obtained. The first *compound* separates in pseudomonoclinic crystals and sublimes at 170—180°. Since the corresponding *amine*, $NH_2 \cdot CMe_2 \cdot CMe_2 \cdot OH$, may be prepared by a trustworthy synthetical method, this compound must have the composition $NO \cdot CMe_2 \cdot CMe_2 \cdot O \cdot NO_2$. The amine forms pseudomonoclinic crystals, melts at 10°, and boils at 160—161° under 254 mm. pressure. The *compound* $NO_2 \cdot CMe_2 \cdot CMe_2 \cdot O \cdot NO_2$ separates in crystals which are unlike those of either of the other compounds, and melts at 88—89°. The third *compound*, $NO_2 \cdot O \cdot CMe_2 \cdot CMe_2 \cdot O \cdot NO_2$, is also obtained by the action of nitric anhydride on tetramethylethylenic oxide, and when reduced with zinc dust and acetic acid yields pinacone hydrate, whilst by the action of tin and hydrochloric acid pinacoline and ammonia are formed; it combines with hydrogen bromide to form tetramethylethylenic bromide, $C_6H_{12}Br_2$. The *compound* $(C_4H_8O_3N_2)_2$, prepared by the action of nitric anhydride on dimethylethylene, crystallises in colourless, pseudomonoclinic prisms, melts at 133—134°, and is insoluble in water. By varying the conditions of the experiment, a product may be obtained which, when reduced with tin and hydrochloric acid, yields methyl ethyl ketone and a *compound*, $OH \cdot CHMe \cdot COMe$, which distils over, whilst the residue contains
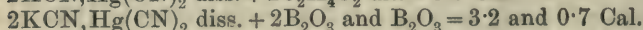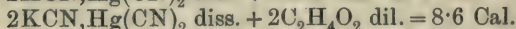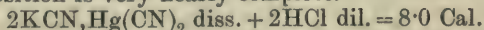
tetramethylpyrazine $\begin{array}{c} \text{CMe·N·CMe} \\ \| \quad | \quad \| \\ \text{CMe·N·CMe} \end{array}$, a compound also formed by reducing the product of the action of nitric peroxide on dimethylethylene; it melts at 86° and boils at 189—190°.   E. W. W.

Double Cyanides. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1899, **17**, [vii], 458—470).—Potassium silver cyanide is completely decomposed by nitric acid (1 mol. in 2 litres); the reaction (AgCN,KCN diss. + HNO₃ dil. = AgCN + KNO₃ diss. + HCN diss.) develops 4·2 Cal.; an excess of the acid has no further action on silver cyanide.

Hydrochloric acid also precipitates silver cyanide from the double salt, but if the acid is in excess, the precipitate consists of a mixture of silver chloride and cyanide; this is explained by the fact that the heats of neutralisation of hydrochloric and hydrocyanic acids by silver oxide are 20·6 Cal. and 21·4 Cal. respectively. The double salt is more stable towards feebler acids, such as acetic, boric, arsenious, and carbonic acids, and behaves like a salt of hydrargentocyanic acid. Carbonic acid has no action on the double salt, although it reacts with potassium cyanide; in the other cases, the heat effect indicates that the decomposition is only partial. The addition of boric acid produces a slight turbidity, and the heat developed is 0·12 Cal.; a similar result is obtained with arsenious acid.

The addition of ½C₂H₄O₂, C₂H₄O₂, or 1½C₂H₄O₂ to a solution of KCN,AgCN develops 1·4, 2·2, or 2·6 Cal. respectively, these thermal effects being accompanied by the partial precipitation of silver cyanide and the liberation of hydrogen cyanide. The quantity of precipitate increases when the reaction is performed in open vessels. The calculated heat effect for complete decomposition is 3·8 Cal.; the values obtained from experiment all fall short of this, and it is assumed that the discrepancy is due to the formation of hydrargentocyanic acid; if this substance were quite stable, there would be no appreciable thermal effect on the addition of the acetic acid; the heat developed is due to its partial dissociation into silver cyanide and hydrogen cyanide. In an open vessel, this dissociation continues, owing to the escape of the hydrogen cyanide; this accounts for the gradual increase of the precipitate. The heat of formation of the hypothetical acid is −3·8 Cal.; its metallic salts form a well-defined series, but there is no thermochemical evidence to show that its silver salt Ag(AgCy₂) differs from ordinary silver cyanide.

Potassium mercuric cyanide is completely decomposed by hydrochloric and acetic acids into mercuric cyanide, hydrogen cyanide, and the potassium salt of the reacting acid; with boric acid, the decomposition is very nearly complete.

2KCN,Hg(CN)₂ diss. + 2HCl dil. = 8·0 Cal.

2KCN,Hg(CN)₂ diss. + 2C₂H₄O₂ dil. = 8·6 Cal.

2KCN,Hg(CN)₂ diss. + 2B₂O₃ and B₂O₃ = 3·2 and 0·7 Cal.

the calculated values for complete decomposition by boric acid being 3·8 Cal. for 2B₂O₃ and 0·9 Cal. for B₂O₃. These results indicate that the hypothetical hydromercuricyanic acid is even more unstable than the corresponding silver compound; its calculated· heat of formation

is $-8\cdot2$ Cal. The mercuric salt of this hypothetical acid is identical with ordinary mercuric cyanide.

Potassium zinc cyanide is completely decomposed by hydrochloric acid; the reaction $2KCN, Zn(CN)_2$ diss. (1 mol. in 4 litres) $+4HCl$ (1 mol. in 2 litres) $= ZnCl_2$ diss. $+2KCl$ diss. $+4HCN$ diss. develops $17\cdot1$ Cal. at $12°$. The decomposition by acetic acid is almost complete; at $12°$, the reaction is accompanied by an evolution of $11\cdot8$ Cal., the calculated value for complete decomposition being 12 Cal. The double zinc salt behaves differently towards hydrogen sulphide, and carbonic and boric acids; these substances produce no immediate precipitation; the heat developed by the addition of boric acid is $1\cdot7$ Cal., the calculated value for complete decomposition being $8\cdot4$ Cal. These results indicate the probable existence of a hydrozincocyanic acid, H_2ZnCy_4, intermediate in stability between the corresponding silver and mercuric compounds; the zinc salt of this acid is, however, identical with ordinary zinc cyanide. G. T. M.

Flash Points of Organic Compounds. By P. N. Raikow (*Chem. Zeit.*, 1899, **23**, 145—147).—The flash points of numerous organic compounds lie below their melting points, for example, benzene, which melts at $+6°$, flashes at $-8°$. The determination of the flash point is suggested as a method for testing the purity of certain organic compounds.

The flash points of aqueous solutions of ethylic alcohol of various concentrations have been determined by the aid of the usual Abel apparatus; some of the numbers obtained are as follows:

Volume per cent. of ethylic alcohol ...	100	90	70	50	30	15	10	4
Flash point	$12°$	$16\cdot5°$	$21°$	$24°$	$29\cdot5°$	$41\cdot75°$	$49°$	$68°$

Although the flash point rises with the dilution of the alcohol, the increment is not proportional to the dilution.

The maximum contraction in volume is obtained when $51\cdot9$ vols. of alcohol are mixed with $48\cdot1$ vols. of water, and as there is no sharp break in the flash point with an alcohol of this concentration, the author argues against the idea of the presence of a definite hydrate in such a mixture. J. J. S.

Non-existence of Monethylic Borate [Metaborate]. By H. Copaux (*Bull. Soc. Chim.*, 1899, [iii], **21**, 776—778).—When boric anhydride is heated with alcohol at $125°$ in an autoclave for 3 hours and excess of alcohol and triethylic borate removed from the product by distillation, a syrupy liquid is obtained which, according to Schiff (*Annalen*, Suppl. 5, 153), is ethylic metaborate, $BO(OEt)$, produced by the action of boric anhydride on the triethylic borate first formed. The results obtained by analysis agree fairly well with this supposition, but the author considers the substance to be a mixture of polymolecular compounds, since (1) it is non-volatile and begins to decompose at $180°$, yielding triethylic borate and a viscous residue; (2) contradictory results are obtained by cryoscopic and ebullioscopic molecular weight determinations, whereas triethylic borate is distinctly shown to be unimolecular; (3) the reaction, assumed by Schiff, between boric

anhydride and triethylic borate could not be obtained; (4) when treated with zinc ethyl or boron fluoride, it yields the same products as are obtained from triethylic borate, namely, boron ethyl, BEt_3, and difluorethylic borate, $BF_2 \cdot OEt$ respectively.   N. L.

Crotonaldehyde. By ERNEST CHARON (*Ann. Chim. Phys.*, 1899, **17**, [vii], 197—288. Compare Abstr., 1896, i, 407, 637, and 661).— The paper contains details of work already published, together with a description of certain new derivatives of crotonaldehyde.

$\beta\gamma$-Dibromobutylic alcohol, $CHMeBr \cdot CHBr \cdot CH_2 \cdot OH$, first obtained by Lieben and Zeisel as a viscid oil, crystallises in colourless prisms melting at 32°; it is readily soluble in ordinary solvents.

a-Chloro-β-butylene (*crotonylic chloride*), $CHMe:CH \cdot CH_2Cl$, prepared by digesting crotonylic alcohol with concentrated hydrochloric acid, is a mobile, colourless liquid boiling at 77° under ordinary pressure, and has a sp. gr. 0·9491 at 0°.

aβγ-Trichlorobutane, $CHMeCl \cdot CHCl \cdot CH_2Cl$, obtained by passing chlorine into a chloroform solution of the preceding compound, is a colourless, oily liquid having an agreeable odour; it boils at 79—80° under 32 mm. pressure, and has a sp. gr. 1·3241 at 0°.

a-Chloro-βγ-dibromobutane, $CHMeBr \cdot CHBr \cdot CH_2Cl$, is a colourless liquid of camphor-like odour; it boils at 93—94° under 15 mm. pressure, and has a sp. gr. 1·9478 at 0°.

a-Bromo-β-butylene (*crotonylic bromide*), $CHMe:CH \cdot CH_2Br$, a liquid resembling allylic bromide, is prepared from crotonylic alcohol and concentrated hydrobromic acid; it boils at 102—103° under ordinary pressure, and has a sp. gr. 1·3119 at 0°. An ethereal solution of this substance, when heated with dry potassium formate, yields *a*γ-butadiene (divinyl), $CH_2:CH \cdot CH:CH_2$.

βγ-Dichloro-a-bromobutane, $CHMeCl \cdot CHCl \cdot CH_2Br$, produced by passing chlorine into a-bromo-β-butylene dissolved in chloroform, is a colourless liquid boiling at 87—88° under 21 mm. pressure, and having a sp. gr. 1·6302 at 0°.

aβγ-Tribromobutane, $CHMeBr \cdot CHBr \cdot CH_2Br$, boils at 113—114° under 21 mm. pressure, and has a sp. gr. 2·2195 at 0°; it is a colourless liquid of camphor-like odour, and reddens on exposure to air.

a-Iodo-β-butylene (crotonylic iodide) is obtained colourless by distillation under diminished pressure; it boils at 61—62° under 50 mm., and has a sp. gr. 1·6823 at 0°. This substance changes spontaneously into a dimeric *polymeride*, $(C_{10}H_7I)_2$, which crystallises in silky needles, sublimes at 100°, and decomposes at 180°.

Octadiene (*dicrotonyl*), $C_2H_4(CH:CHMe)$, is prepared by the action of zinc dust or the copper–zinc couple on crotonylic bromide or iodide; the yield is 40 per cent., and greatly exceeds those obtained by similar reactions in the allylic series. The hydrocarbon is a colourless liquid boiling at 117—119° under ordinary pressure; when treated with iodine, it yields the polymeride of crotonylic iodide.

Methylic crotonylic oxide, $CHMe:CH \cdot CH_2 \cdot OMe$, produced by treating crotonylic bromide with sodium methoxide, is a volatile liquid boiling at 79° under atmospheric pressure, and has a sp. gr. 0·8035 at 0°.

Ethylic crotonylic oxide, prepared in a similar manner to its lower

homologue, boils at 99° under atmospheric pressure, and has a sp. gr. 0·8206 at 0°.

Dicrotonylic oxide, $(CHMe\mathbin{:}CH\cdot CH_2)_2O$, obtained either by mixing sulphuric acid with crotonylic alcohol, or by the action of crotonylic chloride, bromide, or iodide on sodium crotonyloxide, is a colourless liquid having a penetrating odour; it boils at 143—145° under ordinary pressure, and has a sp. gr. 0·8895 at 0°.

Ethylic βγ-dibromobutylic oxide, $CHMe\cdot Br\cdot CHBr\cdot CH_2\cdot OEt$, produced by adding bromine to ethylic crotonylic oxide, boils at 116—117° under 20 mm. pressure, and has a sp. gr. 1·700 at 0°. When this substance is treated with zinc dust, ethylic crotonylic oxide is regenerated.

Dicrotonylic sulphide, $(CHMe\mathbin{:}CH\cdot CH_2)_2S$, results from the action of sodium sulphide on crotonylic bromide; it is a colourless liquid having a garlic odour and burning taste; it boils at 186—187° under ordinary pressure, and at 106—108° under 50 mm.; it has a sp. gr. 0·9032 at 0°.

Crotonylthiocarbimide, produced by warming a methylic alcohol solution of crotonylic bromide and potassium or ammonium thiocyanate, is a colourless liquid with an odour of horseradish; it boils at 83—85° under 50 mm. pressure, and has a sp. gr. 0·9927 at 0°.

Crotonylthiocarbamide, $CHMe\mathbin{:}CH\cdot CH_2\cdot NH\cdot CS\cdot NH_2$, prepared by heating the preceding compound with aqueous ammonia, crystallises from water in colourless scales melting at 105°; it is readily soluble in alcohol or ether.

On mixing crotonaldehyde pinacone (dipropenylic glycol) with bromine in chloroform solutions, two *tetrabromo*-derivatives are obtained; the first crystallises in needles and melts at 123°; the second separates in scales and melts at 171°. The acetyl derivative of the tetrabromo-compounds crystallises in colourless prisms and melts at 141°. When dipropenylic glycol is treated with hypochlorous acid, a *dichlorohydrin*, $C_8H_{16}O_4Cl_2$, is produced; it crystallises in colourless scales melting at 222—223°; the *tetracetyl* derivative of the chlorohydrin melts at 270°.

<div align="right">G. T. M.</div>

Influence of Water on the Velocity of Ether Formation. By CORNELIS A. LOBRY DE BRUYN and ALPHONSE STEGER (*Rec. Trav. Chim.*, 1899, **18**, 311—325).—A study of the reactions NaOEt + MeI and NaOEt + EtI in ethylic alcohol shows that the velocity coefficient decreases as the dilution of the alcohol increases, whilst in the case of the reactions NaOMe + MeI and NaOMe + EtI in methylic alcohol, the addition of water at first produces an increase in the value of the coefficient, which, after attaining a maximum, diminishes continuously as the dilution is increased. Owing to the solubility of methylic iodide in water, it is possible to make experiments under all conditions of dilution, from absolute alcohol to pure water; with the ethylic iodide, it is not possible to employ a medium containing less than 40 per cent. of the alcohol. The velocity coefficient is calculated from determinations of the alkalinity of the solutions after given intervals of time, the temperature being maintained at 25°. The results are tabulated and the variations of the velocity coefficient with change of dilution are represented graphically. It is noticed that when the

dilution is considerable, the value of this coefficient for a given dilution is not constant ; as the reaction proceeds, a gradual diminution becomes apparent ; this may be due to the change in the concentration of the ions, the dissociation of NaOEt or NaOMe being different from that of NaI.

The velocity of the reaction NaOEt + MeI in absolute ethylic alcohol is six times as great as that of NaOMe + MeI in absolute methylic alcohol, although the reagents are far more dissociated in the latter solvent ; moreover, the velocity of the reaction NaOEt + MeI in ethylic alcohol is 30 times greater than that of the reaction NaOMe + EtI in methylic alcohol. It appears, therefore, that the velocity of reactions occurring in media other than water depends, not only on electrolytic dissociation, but also on other undetermined factors.   G. T. M.

Preparation of Formose by means of Amorphous Lead Hydroxide. By CORNELIS A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1899, 18, 309—310).—Amorphous lead hydroxide is precipitated on adding caustic potash to a solution of basic lead acetate ; when dried at ordinary temperatures, it forms a white powder which is more active than lead oxide in promoting the condensation of formaldehyde to formose. A dilute solution of the aldehyde is heated with a small quantity of the hydroxide for one hour at 100° and evaporated down to a syrupy consistence ; the residue is dissolved in a mixture of methylic and ethylic alcohols and treated with ether to precipitate the lead salts of any organic acids present ; the filtrate now contains formose, the yield being about 70 per cent. of the formaldehyde employed. Lead hydroxide, when precipitated by ammonia, appears to be crystalline, and has no action on formaldehyde ; negative results were also obtained with sodium, potassium, zinc, copper, or cadmium hydroxides, whilst 10 per cent. of formose was obtained by the use of calcium hydroxide.

                                           G. T. M.

New Hexosazones from Glycerol and Formaldehyde. By OSCAR LOEW (*Chem. Zeit.*, 1899, 23, 542—543 and 566—567).— Bromine and sodium hydroxide react with glycerol, yielding a mixture of dihydroxyacetone and glyceraldehyde (Fischer and Tafel). Sodium carbonate was employed in place of the hydroxide, the mixture allowed to remain for 12 hours at a low temperature, and the condensation was completed by warming for several days at 55°, until the product gave no deposit of glycerosazone on treatment with phenylhydrazine hydrochloride in acetic acid solution. The condensation product yields an *osazone*, $C_{18}H_{22}O_4N_4$, melting at 157°; it is readily soluble in alcohol, ether, acetone, or ethylic acetate, moderately so in benzene or chloroform ; it also dissolves in about 400 times its weight of boiling water, from which it crystallises in long, felted, thread-like masses. The author terms the compound *morfosazone* on account of its resemblance to formosazone, from which, however, it differs in crystalline habit and in melting point. Morfose is formed, together with formose, when formaldehyde solution is shaken with calcium

hydroxide, filtered, and warmed on the water-bath after the addition of alcohol. At a higher temperature (80°) and in the presence of a smaller quantity of calcium hydroxide, a third sugar is obtained, the osazone of which melts at 167° and somewhat resembles that mentioned by Fenton (Trans., 1897, **71**, 379). When the crude glycerose obtained by the action of bromine and sodium carbonate on glycerol is treated with acetic acid until all the bicarbonate is decomposed, and then with calcium hydroxide, a further condensation ensues, which is complete in 4 hours at 20° or in 5 minutes at 82°. The product yields an osazone, *lycerosazone*, which crystallises from hot water in very characteristic spindle-shaped crystals melting at 152°; it dissolves less readily than formosazone in ether, chloroform, turpentine, or benzene.　　　　　　　　　　　　　　**J. J. S.**

Rotatory Power of Sugar Solutions. By E. Mascart and H. Bénard (*Ann. Chim. Phys.*, 1899, **17**, [vii], 125—144).—The paper contains details of experiments made, at the request of the French Ministry of Finance, with the object of determining accurately the rotatory power of a sugar solution of convenient strength for use in commercial analyses; it is not suitable for abstraction.　　**G. T. M.**

Groups of Carbohydrates. By Venturo Zanotti (*Chem. Centr.*, 1899, i, 1209—1210; from *Ann. Soc. Chim. Milano*, 1899, 27—39). —The shells of nuts contain compounds which yield xylose and dextrose, and whose constitution is very different to that of cellulose. Phenylxylosazone melts at 153°. Generally speaking, dextrin always occurs associated with xylin, and galactin with arabin in plants.

Penicillium glaucum, in common with other low organisms, contains a small quantity of mannin.

When cellulose prepared from purified cotton wool was oxidised by (a) hydrochloric acid and potassium chlorate, (b) chromic and sulphuric acids, (c) potassium permanganate and sulphuric acid, " oxycelluloses " of the following compositions were obtained :

	Oxycellulose.		
	a.	*b.*	*c.*
Ash	0·15	0·50	0·30
Carbon	43·66	42·96	42·52
Hydrogen	6·60	6·52	6·56
Oxygen	49·74	50·52	50·92
Furfuraldehyde	0·80	3·05	1·90
Cellulose	45·20	26·05	39·92
Oxycellulose, by difference	54·80	73·95	60·08

The action of alkalis showed that these substances are really mixtures of cellulose and hydrocellulose with their oxidation and decomposition products.　　　　　　　　　　　　　**E. W. W.**

Molecular Weight of Soluble Starch. By H. Friedenthal (*Chem. Centr.*, 1899, i, 924; from *Centr. Physiol.*, **12**, 849—850).— By dissolving " ozone-starch," a commercial soluble starch, in water and precipitating with alcohol, a product was obtained the molecular

weight of which was found by Beckmann's method to be 9450. The empirical formula of the starch being $3C_6H_{10}O_5 + H_2O$, this result would indicate a molecular formula 20 $(C_{18}H_{30}O_{15} + H_2O)$, but the formula 60 $C_6H_{10}O_5 + H_2O$ corresponds still better with the number obtained.   E. W. W.

Combination of Colloidal with Crystalloidal Substances. By A. FRIEDENTHAL (*Chem. Centr.*, 1899, i, 1161—1162 ; from *Centr. Physiol.*, **13**, 54—58).—The addition of 1 per cent. of iodine to a 5 per cent. solution of starch does not lower the freezing point of the solution by a measurable amount, hence iodide of starch would appear to be a chemical compound rather than a simple solution. The freezing point of a solution of iodine in potassium iodide, however, is considerably lowered by adding large quantities of soluble starch. The varying results obtained by the author and by Küster indicate that this method is not applicable in the case of starch, just as physico-chemical methods give untrustworthy results with compounds of such high molecular weight as albumin and albumoses, since the least quantity of ash causes great errors.   E. W. W.

Cellulose and Starch. By ZDENKO H. SKRAUP (*Ber.*, 1899, **32**, 2413—2414).—Franchimont found that cellulose yields acetyl compounds when treated with a mixture of acetic anhydride and sulphuric acid, and that one of these is crystalline, and has the composition of a triglucose containing 11 acetyl groups.

It has been found that if low temperatures and small quantities of sulphuric acid are used, the products are more complicated than when these precautions are not observed.

[With HUGO HAMBURGER.]—Starch, on moderated acetylation, gives an acetyl compound which, when hydrolysed with alkalis, yields a product having all the characteristic properties of soluble starch. On energetic acetylation, however, breaking down occurs, attended by addition of acetic anhydride, and besides amorphous products, pentacetylglucose melting at 113° is obtained ; this, however, is only produced when the product is treated with water.

[With PREGL.]—Cellulose, when energetically acetylated, yields, by addition of acetic anhydride, a substance which crystallises from ethylic acetate or alcohol in beautiful, long needles melting at 228°, and is identical with Franchimont's substance ; determination of the molecular weight of the compound, however, shows that his view of its constitution is incorrect, and that it is either a pentacetylhexose or a heptacetylheptose. On hydrolysis with alkali, it does not yield glucose, but a substance sparingly soluble in alcohol although readily soluble in water, which gives, not an osazone, but a phenylhydrazone melting at 194°, and closely resembling mannosephenylhydrazone in many particulars.

By very careful acetylation, cellulose and starch yield derivatives which contain more acetyl than might be anticipated on the basis of the usual formulæ for these substances.   A. L.

Cellulose. By G. BUMCKE and RICHARD WOLFFENSTEIN (*Ber.*, 1899, **32**, 2493—2507).—The so-called oxycellulose, obtained by treat-

ing cellulose with hydrogen peroxide, possesses many of the properties usually associated with aldehydes ; it is strongly reducing, combines with phenylhydrazine, and restores the colour to a solution of magenta and sulphurous acid. Cellulose itself is destitute of these properties, and the fact that oxycellulose behaves like a reducing agent tells against the view that the action is one of oxidation ; here, as in the case of cane sugar (Wurster, *Centr. Physiol.*, 1, 33), hydrogen peroxide acts as a hydrolytic agent. Ash-free filter paper was treated at ordinary temperatures with varying quantities of re-distilled hydrogen peroxide (4 to 60 per cent.) until the fibres were completely disintegrated. Analyses of the dried product gave numbers corresponding with $6C_6H_{10}O_5,H_2O$, $7C_6H_{10}O_5,H_2O$, or $8C_6H_{10}O_5,H_2O$; the analytical results are not conclusive, owing to the molecular complexity of the substances involved. This product the authors call *hydralcellulose ;* it has no action on iodine solution, but when treated with excess of phenylhydrazine, it yields a hydrazone containing 1·69 to 1·83 per cent. of nitrogen : a phenylhydrazone having the composition $C_{36}H_{62}O_{30}$·N_2HPh should contain 2·6 per cent. Cellulose itself is not acted on by phenylhydrazine. The hydrazone partly dissolves in caustic soda solution, but the soluble and insoluble portions alike contain the same percentage of nitrogen. When tested with Fehling solution, the reducing power of hydralcellulose is found to be 1/12th that of dextrose. On acidifying the solution of hydralcellulose in this reagent, a flocculent, white precipitate is obtained ; this product, "*acid-cellulose*," is also produced by warming hydralcellulose with excess of 10 per cent. caustic soda solution ; the yield is about 33 per cent., an insoluble substance having the properties of cellulose being formed at the same time ; the reaction appears to be quite analogous to the action of alkalis on certain aldehydes ; hydralcellulose (aldehyde) = cellulose (alcohol) + acid-cellulose (acid). Acid-cellulose may also be prepared directly from cellulose, either by heating this substance with a 30 per cent. solution of caustic soda until the whole has passed into solution, or by acidifying the solution of cellulose in Schweitzer's reagent ; in the former process, the yield is 39 per cent., in the latter, the substance is accompanied by a small amount of hydralcellulose.

Acid-cellulose readily dissolves in dilute alkalis, but not in aqueous ammonia ; it has an acid reaction, decolorising an alkaline solution of phenolphthalein, and does not react with Fehling's solution, phenylhydrazine, or iodine solution ; when left in contact with concentrated hydrochloric acid, it undergoes hydrolytic decomposition into soluble products which have reducing properties. When dried at 105°, acid-cellulose loses water and becomes converted into *acid-celluloselactone*, $C_{36}H_{60}O_{31}$; this substance forms a hard, horny mass insoluble in alkalis.

The action of concentrated nitric acid on cellulose is not simply one of nitration, hydrolytic changes are simultaneously produced so that the same products are obtained by nitrating cellulose, hydralcellulose, and acid-celluloselactone. The dried substance was in each case mixed with 10 parts of nitric acid of sp. gr. 1·48 and heated for some time at 85° ; the product was soluble in acetone and was separated

into two fractions differing in solubility in ethylic alcohol. The more soluble substance forms a friable mass, whilst the other is obtained in coherent films. Both substances, derived either from cellulose, hydralcellulose, or acid-cellulose prepared by Schweitzer's reagent, have the same composition, and gave analytical numbers agreeing with the formula $\{\frac{2}{3}C_{72}H_{106}O_{44}(NO_3)_{18}, \frac{1}{3}C_{72}H_{112}O_{50}(NO_3)_{12}\}$; the more soluble nitro-derivative obtained from the acid-celluloselactone, prepared with cellulose and caustic soda solution, also had this composition, but the less soluble substance contained more of the dinitro-compound. The more soluble substance was further identified by determining its rotatory power in acetone solution and its exploding point. The molecular weight determined in acetone solution by the ebullioscopic method showed that the molecular complexity of the nitro-compound, whether obtained from cellulose, hydralcellulose or acid-celluloselactone, is the same, namely, 1350. The experimental results indicate that the formula for hydralcellulose is probably $6C_6H_{10}O_5, H_2O$, and if the foregoing explanation of its formation from cellulose be accepted, the latter substance should have the formula $C_{72}H_{120}O_{60}$. G. T. M.

Oxycellulose. By O. von FABER and BERNHARD TOLLENS (*Ber.*, 1899, **32**, 2589—2601).—The oxycelluloses obtained from cellulose by the action of various oxidising agents appear to consist of varying proportions of unaltered cellulose and a substance, $C_6H_{10}O_6$ or $C_6H_8O_6$, containing an additional oxygen atom, for which the name *celloxin* is proposed. This compound has not been isolated, but on heating oxycellulose with lime water, it is decomposed into a mixture of isosaccharinic and dihydroxybutyric acids, whilst the cellulose remains unaltered.

Pine-wood sawdust, when heated with moderately concentrated nitric acid for 6 hours, yields a white powder having a composition corresponding with either the formula $C_{18}H_{28}O_{16}$ or $C_{18}H_{30}O_{16}$; when the action is stopped after 3 hours, the composition of the powder obtained agrees with $C_{24}H_{38}O_{21}$ or $C_{24}H_{40}O_{21}$. On distilling with hydrochloric acid, these substances yield about 7 per cent. of furfuraldehyde. The product, obtained by treating cotton wool with bromine and calcium carbonate, forms a white powder which reduces Fehling's solution, develops a violet coloration with iodine and zinc chloride, restores the colour to magenta decolorised by sulphurous acid, and is insoluble in dilute alkalis or ammonia ; it corresponds in composition with the formula $C_{12}H_{20}O_{11}$ $(C_6H_{10}O_5 + C_6H_{10}O_6)$, and on distillation with hydrochloric acid yields about 1·6 per cent. of furfuraldehyde. The composition of the white powder, obtained by heating cotton wool with nitric acid of sp. gr. 1·3 for 2½ hours on the water-bath, corresponds either with $C_{30}H_{48}O_{26}$ or $C_{30}H_{50}O_{26}$; when the action is continued for 4 hours, the composition of the product agrees with either $C_{24}H_{38}O_{21}$ or $C_{24}H_{40}O_{21}$. In the first case, the product appears to contain 4 mols. of cellulose to 1 mol. of celloxin, and in the second case the proportions are 3 : 1. The oxycelluloses, prepared by the action of nitric acid, dissolve in dilute alkalis or ammonia to form viscid solutions having reducing properties, and differ in this respect from that obtained by the aid of bromine and calcium carbonate ; all these substances, when warmed with caustic

soda, give golden-yellow solutions which reduce Fehling's solution. As the proportion of celloxin becomes greater, the solubility in dilute alkalis and the reducing power increase (compare preceding abstract). All the oxycelluloses obtained by the methods described above, when boiled with milk of lime, undergo decomposition, the celloxin being converted into the calcium salts of isosaccharinic and dihydroxybutyric acids, whilst the cellulose remains undissolved. The former acid is isolated by means of its calcium salt, which, on treatment with acids, yields iso-saccharin melting at 92—94°, but having a specific rotatory power of 49·4° (not 62—63°, as usually stated). Dihydroxybutyric acid, when liberated from a solution of the calcium salt by oxalic acid, has at first a specific rotatory power of $-2\cdot6°$ which after 2 days becomes $+13\cdot7°$. In preparing oxycelluloses by the action of nitric acid on cotton wool, saccharic acid and other acids containing 4 or 5 atoms of oxygen are produced as bye-products. G. T. M.

Action of Methylic Chloride, Bromide, and Iodide on Ammonia. By B. Dübowsky (*Chem. Centr.*, 1899, i, 1066; from *J. Russ. Chem. Soc.*, 1899, **31**, 34—37. Compare Menschutkin, Abstr., 1895, ii, 385).—The action of a 35 per cent. solution of ammonia in methylic alcohol on methylic chloride, methylic bromide, or methylic iodide dissolved in 3—4 volumes of toluene is complete in 4 months at the ordinary temperature and products are formed which contain an amount of halogen corresponding with methylamine hydrochloride, hydrobromide, and hydriodide respectively. The same reaction takes place in 2—3 minutes at 100°. The amines obtained from these products, however, when treated with methylic bromide, yield compounds containing less bromine than that required for dimethylamine hydrobromide, &c., and from the products of the original reaction, ammonium chloride, bromide, or iodide respectively may be separated by fractionally crystallising from alcohol; the amounts of tetramethylammonium compounds are estimated by titrating the alcoholic solutions with alcoholic sodium hydroxide solution. The hydrochloride was found to contain 75·2 per cent. of ammonium and amine salts and 24·8 of tetramethylammonium chloride, the hydrobromide of 75·7 of ammonium and amine salts and 24·3 of tetramethylammonium bromide, and the hydriodide of 75·6 of ammonium and amine salts and 24·4 of ammonium iodide.

E. W. W.

A New Amylamine. By D. Trasciatti (*Gazzetta*, 1899, **29**, ii, 92—101).—On reducing isonitrosodimethylethylcarbinylic cyanide, $CN\cdot CMe_2\cdot CMe:NOH$ (Guthrie's salt), in alcoholic solution by means of sodium, an amylamine, *αβ-dimethylpropylamine*, $CHMe_2\cdot CHMe\cdot NH_2$, is obtained as a colourless liquid which boils at 84—87° and has a disgusting smell. Its *hydrochloride*, $C_5H_{13}N,HCl$, crystallises from alcohol in slender, silky, deliquescent needles. It forms two *oxalates*, the first, which has the composition $C_5H_{13}N,H_2C_2O_4$, crystallises from alcohol in sparkling, white needles; the other, $(C_5H_{13}N)_2,H_2C_2O_4$, forms a white, crystalline mass which dissolves readily in water and decomposes without melting at 220°.

The action of nitrous acid on the amylamine gives rise to methylisopropylcarbinol.   T. H. P.

Constitution of Inorganic Compounds. XVIII. Compounds of Ethylenediamine and Propylenediamine with Salt of Bivalent Metals. By ALFRED WERNER, W. MEGERLE, J. PASTOR, and W. SPRUCK (*Zeit. anorg. Chem.*, 1899, **21**, 201—242).—*Triethylenediaminenickel salts.*—The *sulphate*, $[Ni(C_2H_8N_2)_3]SO_4$, obtained by adding ethylenediamine (3 mols.) to a concentrated solution of nickel sulphate (1 mol.), crystallises from boiling water in beautiful needles and is insoluble in alcohol. A determination of the molecular weight by the cryoscopic method gave 159·8, the theoretical number being 167·4 ; the molecular electric conductivity for $v = 1000$ is 224·4, which agrees with the molecular conductivity of chloropentammine cobalt sulphate, and shows that triethylenediaminenickel sulphate is soluble in water without decomposition. The *nitrate* crystallises in dark violet tablets, is somewhat easily soluble in water, and, according to the cryoscopic determinations, is then dissociated into the three ions, $Ni(C_2H_8N_2)_3$ and $2NO_3$. The *chloride* crystallises in small, violet dihydrated prisms, the *bromide* in violet dihydrated, efflorescent leaflets, and the *iodide* in insoluble, monohydrated, reddish-violet prisms and plates. *Triethylenediaminenickel platinochloride*, $[Ni(C_2H_8N_2)_3]PtCl_6$, is an amorphous, brownish-yellow precipitate and is insoluble in water.

Tripropylenediaminenickel salts differ from the triethylenediamine salts in that they are extremely soluble in water. The *sulphate*, $[Ni(C_3H_{10}N_2)_3]SO_4$, is obtained by heating powdered nickel sulphate with the theoretical quantity of propylenediamine until a dark violet salt is obtained. It is a peach-coloured, microcrystalline powder, and gives precipitates with alkali chlorides, bromides, iodides, cyanides, or thiocyanates. The *chloride* crystallises in dihydrated, beautiful, reddish-violet leaflets, the *bromide* in dihydrated bright reddish-violet needles, the *iodide* in dihydrated reddish-violet needles, the *thiocyanate* in sparingly soluble, reddish-violet needles, and the *cyanide* in sparingly soluble, bright rose needles.

Triethylenediaminecopper salts are less stable than the other salts of the hexammine series, and the third ethylenediamine molecule is eliminated when they are dissolved in water ; they can, however, be recrystallised from very concentrated solutions with only partial decomposition. The *sulphate*, crystallises in beautiful, blue needles and is slightly hygroscopic ; the *nitrate* forms dihydrated, bluish-violet leaflets, and is not so readily decomposed by water as the sulphate.

Triethylenediaminezinc salts.—The *sulphate* crystallises in easily soluble, short, white needles, the *nitrate* in very hygroscopic, thick, colourless needles, the *chloride* in needles, the *bromide* in large, thick plates, and the *iodide* in pale yellow forms.

Triethylenediaminecadmium salts.—The *sulphate* crystallises in moderately soluble aggregates of lustrous prisms, and the *nitrate* in very hygroscopic, white crystals. The *chloride* crystallises in easily soluble white needles, the *bromide* in tablets, and the *iodide* in sparingly soluble, thick, prismatic needles.

Triethylenediaminecobalt sulphate, obtained as a yellowish, flesh-

coloured magma on adding ethylenediamine to a solution of cobalt sulphate, cannot be recrystallised on account of the ease with which it is oxidised, and is sparingly soluble in water.

Tetrammine salts. Diethylenediaminenickel salts.—The *bromide*, $[\text{Ni}(C_2H_8N_2)_2]Br_2 + 2H_2O$, is obtained by adding diethylenediamine (2 mols.) to a solution of nickel bromide; it crystallises in blue leaflets, is easily soluble in water, effloresces on exposure to the air, and when treated with potassium cyanide is converted into triethylenediaminenickel bromide. The *iodide* crystallises in aggregates of greyish-blue leaflets, and is easily soluble in water. The *thiocyanate*, obtained by treating the bromide with potassium thiocyanate, occurs in two isomeric forms, the one separates at once as a violet-red precipitate, the other crystallises from the mother liquor in deep, bluish-violet, six-sided plates. Both compounds can be readily recrystallised from water.

Dipropylenediaminenickel salts.—When propylenediamine (2 mols.) is added to a concentrated solution of nickel sulphate, a deep blue solution is obtained, from which the following salts can be prepared. The *bromide*, with $2H_2O$, is obtained, together with a bright blue salt, by evaporating the above solution with potassium bromide almost to dryness and then extracting the blue salt mechanically; it crystallises in reddish-blue nodules, and becomes green when dried in a desiccator. The *thiocyanate* is a violet-red salt, sparingly soluble in cold, easily so in hot water, and soluble in alcohol or ether.

Diethylenediaminecopper salts.—The *sulphate* obtained by precipitating a dilute solution of triethylenediaminecopper sulphate with alcohol, is a violet, microcrystalline salt, and is very easily soluble in water. The *chloride* crystallises in large, reddish-blue leaflets, and is easily soluble in water.

Dipropylenediamineplatinous chloride, obtained by adding propylenediamine to a solution of potassium platinosochloride and boiling the mixture in a reflux apparatus until the yellow precipitate is almost completely dissolved, crystallises in greyish-white leaflets containing water. A solution of the *base* is obtained by shaking it with freshly precipitated silver oxide; it has a strongly alkaline reaction, absorbs carbonic anhydride from the air, and has all the properties of a caustic alkali. The *bromide* crystallises in snow-white leaflets containing water, is easily soluble in water, and gradually becomes indigo-blue. The same indigo-blue salt is obtained by adding bromine to a solution of the bromide; it is a new member of the characteristic additive products of platinoso- and platini-salts, and yields a colourless solution in water. The *iodide* separates in small, indefinite crystals, and is extremely soluble.

Dichlorodipropylenediamineplatinic chloride, $[\text{PtCl}_2(C_3H_{10}N_2)_2]Cl_2$, is obtained by the action of chlorine on an aqueous solution of dipropylenediamineplatinous chloride, and crystallises in yellowish prisms.

Dibromodipropylenediamineplatinic chloride, obtained in a similar manner to the preceding salt, separates in yellow crystals and is easily soluble in water.

Propylenediaminediammineplatinous chloride,

$$[\text{Pt}(NH_3)_2(C_3H_{10}N_2)_2]Cl_2,$$
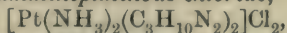
is obtained by cautiously adding ammonia to propylenediaminedichloro-

platinum (see later), suspended in boiling water, until a clear solution is obtained, and, after boiling off the excess of water, adding potassium platinosochloride. It is an insoluble, lilac, microcrystalline salt.

Dibromopropylenediaminediammineplatinic chloride, obtained by treating the preceding compound with bromine, is precipitated from the solution by alcohol and ether, or by acetone, and separates from water, in which it is extremely soluble, in beautiful, yellow crystals.

Diammine salts.—*Tetraquoethylenediaminenickel sulphate,*

$$[Ni(C_2H_8N_2)(H_2O)_4]SO_4 + 1H_2O,$$
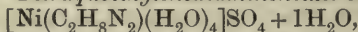
obtained by adding ethylenediamine to a solution of nickel sulphate until triethylenediaminenickel sulphate begins to separate and then concentrating the blue solution in a vacuum, crystallises in pure blue tablets, or rosettes of needles, and is sparingly soluble in cold, easily so in hot water.

Propylenediaminenickel thiocyanate, $[Ni(C_3H_{10}N_2)](SCN)_2 + H_2O$, obtained from the mother liquor in the preparation of the dipropylenediamine salt, or by adding potassium thiocyanate to a solution of nickel sulphate and propylenediamine, in molecular proportion, is a greyish-blue, crystalline powder easily soluble in water.

Dichloropropylenediamineplatinum, $[Pt(C_3H_{10}N_2)]Cl_2$, obtained as a dirty yellow precipitate by adding propylenediamine to a solution of potassium platinosochloride, crystallises from hot water in beautiful, bright yellow needles.

Tetrachloropropylenediamineplatinum, $[Pt(C_3H_{10}N_2)Cl_4$, obtained by treating the preceding compound with chlorine, separates in beautiful, lemon-yellow, flat crystals, and is easily soluble in water. When treated with propylenediamine, it yields a white, and a bright yellow, salt, which can be separated by fractional crystallisation, and are probably isomeric dichlorodipropylenediamineplatinic chlorides.

E. C. R.

Preparation of Hydrazides and their Transformation Products. By Guido Pellizzari (*Real. Accad. dei Lincei,* 1899, **8,** 327—332).—Dibenzohydrazide can be obtained in almost theoretical yield by the action of benzoic chloride on a potassium hydroxide solution of hydrazine sulphate; crystallised from alcohol, it forms white plates melting at 238° (Curtius and Struve gave the melting point 233°). When heated at about 280° for 6 hours, it is converted mainly into diphenyldiazoxole, a small quantity of 3 : 5-diphenyltriazole being also formed.

Diacetohydrazide, $N_2H_2Ac_2$, prepared by the action of acetic anhydride on monacetohydrazide or on a mixture of hydrazine sulphate and dry sodium acetate, crystallises from alcohol in slender needles melting at 140°. From aqueous alcohol, it separates, with $1H_2O$, in the form of colourless plates melting between 80° and 100°.

Diformohydrazide is obtained on heating hydrazine sulphate with dry sodium formate.

When heated, monacetohydrazide loses water, giving *dimethyltetrazoline,* which crystallises in prisms, melts at 196°, and, on boiling with acetic anhydride, yields the monaceto- and with difficulty the diaceto-hydrazide. Diacetohydrazide, when heated, gives rise to

monacetodimethyltetrazoline, which forms prismatic crystals and melts at 163°. Diformohydrazide gives a non-crystallisable product, which, with hydrochloric acid, evolves formic acid and yields *tetrazoline* [*dihydrotetrazine*]·*hydrochloride*, $NH{<}^{CH:N}_{N:CH}{>}NH,HCl$, crystallising in transparent laminæ and melting at 150°.　　　　　　　　T. H. P.

Chloranhydride of Allylphosphorous Acid. By M. PODLADT-SCHIKOFF (*Chem. Centr.*, 1899, i, 1067; from *J. Russ. Chem. Soc.*, 1899, **31**, 30—33).—By the action of phosphorus pentachloride on allylic alcohol, *allylphosphorous chloride*, $CH_2{:}CH{\cdot}CH_2{\cdot}O{\cdot}PCl_2$, and about 9 per cent. of allylic chloride are formed. The former boils at 140·5° under 742·5 mm. pressure, has a sp. gr. 1·29003 at 0°/0° and 1·2685 at 18°/0°. By the action of bromine, it yields allylic bromide, phosphoryl bromochloride, and by the action of chlorine, allylic chloride and phosphorus oxychloride. When a mixture of allylphosphorous chloride and iodine is placed in a sealed tube and exposed to the light, decomposition takes place, carbon and hydrogen iodide being formed; the same action takes place in the dark at 100°.　　　　　　　　E. W. W.

Thioacetaldehydes. By HEINRICH KLINGER (*Ber.*, 1899, **32**, 2194—2195).—Autenrieth and Wolff (this vol., i, 580) are in error in ascribing the elucidation of the cyclic structure of trithioaldehydes to Baumann; the latter has expressly attributed it to the author (Abstr., 1891, 1009).

The isomerism of the thioaldehydes is of a kind in which the isomerides have the same molecular weight and chemical structure, but different amounts of energy. For such isomerism, the author would prefer the name *dynamical isomerism*, were that not already appropriated; as it is, he proposes the term *alloergatia*. Malic and fumaric acids form the classical example of this kind of isomerism.

Liquid thioacetaldehyde, which is formed when hydrogen sulphide is continuously passed into aqueous aldehyde, has the composition $8 CH_3{\cdot}CHS,H_2S$. With alkalis, it reacts like a hydrosulphide; by strong sulphuric acid and other reagents, it is converted into α- or β-trithioacetaldehyde; when distilled, it yields ethylic bisulphide along with hydrogen sulphide and volatile sulphides and hydrosulphides, whilst a carbonaceous residue remains in the flask.　　　　　C. F. B.

Acetone Oils. By R. DUCHEMIN (*Bull. Soc. Chim.*, 1899, [iii], **21**, 798—800. Compare this vol., i, 475, 476).—The composition of acetone oil varies considerably, as is shown by the results obtained from seven different samples. The differences observed are due partly to variations in the composition of the calcium pyrolignate, which forms the original source of the oil, and partly to the more or less complete washing to which it has been subjected. Far from being always rich in methyl propyl ketone and methyl isopropyl ketone, some specimens of the oil contain only traces of these substances, and, on the other hand, as much as 50 per cent. of ketones, more especially methyl ethyl ketone, distilling below 90°.　　　　　　　　N. L.

Dibromopinacolin. By IWAN L. KONDAKOFF (*Chem. Zeit.*, 1899, **23**, 311).—The compound previously (*J. pr. Chem.*, 1896, [ii], **54**, 429)
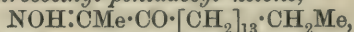
obtained by the action of concentrated hydrobromic acid on pinacone, and stated to melt at 72°, proves to be *dibromopinacolin*, probably having the constitution $CH_2Br \cdot CO \cdot CMe_2 \cdot CH_2Br$. It crystallises from light petroleum in large, colourless prisms melting at 73·5—74° and has a slightly irritating odour. The same product may be obtained by the action of bromine on pinacolin (compare Scholl and Weil, *Chem. Zeit.*, 1899, **23**, 189).   J. J. S.

Methyl Nonyl Ketone. By HENRI CARETTE (*J. Pharm.*, 1899, [vi], **10**, 255—257).—The ketone was obtained from commercial essence of rue. Its compound with ammonium hydrogen sulphite forms nacreous crystals which are insoluble in water but very soluble in alcohol, and when heated with water yield the pure ketone. *Methyl nonyl ketone* boils at 226° (230·65° corr.) under 766 mm., and at 121—122° (122—123° corr.) under 24 mm. pressure, the *oxime* forms elongated prisms, sometimes 6 cm. long, which melt at 46° and are insoluble in water but very soluble in alcohol, ether, benzene, chloroform, or toluene.   H. R. LE S.

Molecular Aggregation of Dihydroxyacetone. By GABRIEL BERTRAND (*Compt. rend.*, 1899, **129**, 341—344).—Dihydroxyacetone, obtained by the action of the sorbose bacterium on glycerol (Abstr., 1898, i, 556), crystallises from its aqueous solution in a vacuum in small prisms which remain unchanged in closed vessels, but liquefy after some time if exposed to the air. The crystals are insoluble in cold absolute alcohol, ether, or acetone, but dissolve in any proportion in the boiling liquids and do not separate when the solution is cooled. The crystals melt slowly at about 70° and remain in superfusion for a considerable time; the superfused, and therefore amorphous, mass, dissolves immediately in cold absolute alcohol, acetone, or ether.

Cryoscopic determinations show that when the crystals are dissolved in water at 5° the molecular weight of the substance gradually changes from about 162 to 91. If, however, the superfused substance is dissolved, its molecular weight in solution is but little higher than 90. The molecular weight of the dissolved substance is higher the lower the temperature. If the solution is heated to 100° and then rapidly cooled, the molecular weight is 88—89, but gradually increases to 91—93 if it is allowed to remain at the ordinary temperature. These facts indicate that in crystallised dihydroxyacetone two molecules of the simple substance are aggregated together and that these are more or less completely separated when it is dissolved or fused.   C. H. B.

Transformation of Ketones into *α*-Diketones. IV. By GIACOMO PONZIO and AUSONIO DE GASPARI (*Gazzetta*, 1899, **29**, i, 471—476).—*Isonitrosoethyl pentadecyl ketone*,
$$NOH \text{:} CMe \cdot CO \cdot [CH_2]_{13} \cdot CH_2Me,$$
prepared by the action of isoamylic nitrite on an ethereal solution of ethyl pentadecyl ketone in presence of hydrochloric acid, crystallises from light petroleum in very slender needles melting at 79—80°, and dissolves in the cold in alcohol, ether, or benzene, but is insoluble in water; it dissolves in hot sodium or potassium hydroxide solution,

giving a yellow liquid from which it separates out unchanged on cooling. When treated with hydroxylamine hydrochloride, in molecular proportion, in presence of sodium hydroxide, it is converted into *acetylpalmityldioxime*, $NOH:CMe \cdot C(NOH) \cdot [CH_2]_{13} \cdot CH_2Me$, which crystallises from alcohol in slender needles melting at $147—148°$ and dissolves in cold ether or hot benzene, but is almost insoluble in light petroleum.

The action of nitric acid on ethyl pentadecyl ketone gives rise to dinitroethane, palmitic acid, and isonitrosoethyl pentadecyl ketone.

Ethyl heptadecyl ketoxime, $CH_2Me \cdot C(NOH) \cdot [CH_2]_{15} \cdot CH_2Me$, crystallises from alcohol in needles melting at $55·5—56·5°$, and is fairly soluble in ether or acetone, but only slightly so in cold alcohol or light petroleum.

Isonitrosoethyl heptadecyl ketone, $NOH:CMe \cdot CO \cdot [CH_2]_{15} \cdot CH_2Me$, crystallises from light petroleum in silky needles melting at $80—81°$, and is fairly soluble in cold alcohol, benzene, or ether. With hydroxylamine hydrochloride, it gives *acetylstearyldioxime*,

$$NOH:CMe \cdot C(NOH) \cdot (CH_2)_{15} \cdot CH_2Me,$$
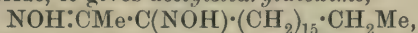
which separates from alcohol in slender needles melting at $120—121°$, and is soluble in the ordinary organic solvents except cold light petroleum, in which it is almost insoluble. With nitric acid, ethyl heptadecyl ketone yields dinitroethane, stearic acid, and isonitrosoethyl heptadecyl ketone. T. H. P.

Relative Strengths of Acids. By CORNELIS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1899, 18, 298—301).—Congo red papers, prepared by soaking blotting paper in a dilute alcoholic solution of the dye, are used in demonstrating qualitatively the relative strengths of acids, the concentration of the acid solutions employed varying from $N/10$ to N. The colour changes to various shades of violet and blue, the strongest acids producing the bluest shades. In this way, differences may be observed between acetic and formic, glycollic, lactic, and propionic acids; also between succinic and maleic and dibromosuccinic acids. The increase in strength resulting from the successive addition of chlorine may be shown in the case of acetic acid and its chloro-derivatives; the increase due to the substitution of hydrogen by hydroxyl is indicated by succinic, malic, and tartaric acids, whilst a gradual decrease of acidity is observed with the following series: oxalic, malonic, and succinic acids. G. T. M.

Chlorostearic Acid. By ALEXIUS ALBITZKY (*Chem. Centr.*, 1899, i, 1070; from *J. Russ. Chem. Soc.*, 1899, 31, 100—103).—Chlorostearic acid could not be prepared by Piotrowski's method of passing hydrogen chloride into a solution of oleic or elaidic acid and allowing the product to remain at the ordinary temperature (Abstr., 1890, 1396), but it was obtained when the mixture was heated at $150°$ for seven hours. Chlorostearic acid crystallises from ether in small nodules, and melts at $38—41°$; on cooling, the molten mass undergoes conversion into a modification which melts at $20—22°$, and gradually changes into the original acid. By the action of potassium hydroxide on the chlorostearic acid obtained either from oleic or elaidic acid, the same hydroxystearic acid is formed. E. W. W.

Action of Acetic Anhydride on Fatty Acids. By ALEXIUS ALBITZKY (*Chem. Centr.*, 1899, i, 1070; from *J. Russ. Chem. Soc.*, 1899, **31**, 103—106).—When palmitic acid is heated with an equal weight of acetic anhydride at 150° for six hours, palmitic anhydride melting at 55—56° is obtained. Stearic anhydride, prepared from stearic acid in a similar manner, melts at 71—77°. Oleic acid yields only an impure *oleic anhydride* which melts at 22—24°, and erucic acid an *anhydride* melting at 47—50°. This reaction may be used generally for the preparation of the anhydrides of the higher fatty acids, hence in Benedikt and Ulzer's method of determining the hydroxyl groups in hydroxy-acids (*Ber. Akad. Wiss. Wien*, **95**, [ii], 110), after hydrolysing the acetyl compound, it is necessary to distil off the acetic acid.   E. W. W.

Oleic Acid. By WILHELM FAHRION (*Chem. Zeit.*, 1899, **23**, 770).— A specimen of pure oleic acid, which had been kept in a glass bottle for some three years, contained a substance insoluble in alkali. This is best extracted by shaking the neutral aqueous alcoholic solution with light petroleum. The amount of this neutral substance was about 5·53—5·67 per cent., its iodine number 53·3—54·8; it appeared, however, to be a mixture of a crystalline substance and an oil, the latter having the same percentage composition as oleic acid.   J. J. S.

Isomerism of Oleic and Elaidic Acids, and of Erucic and Brassidic Acids. By ALEXIUS ALBITZKY (*Chem. Centr.*, 1899, i, 1068—1070; from *J. Russ. Chem. Soc.*, 1899, **31**, 76—100).— Chlorohydroxystearic acids were prepared from oleic, iso-oleic, and elaidic acids, and chlorohydroxybehenic acids from erucic, iso-erucic, and brassidic acids by means of the additive compounds formed with hypochlorous acid. In most cases, it was impossible to obtain a pure product, and the partially purified compound was used in the following reactions. By the action of aqueous or alcoholic potash on the chlorohydroxystearic acid prepared from elaidic acid, the dihydroxystearic acid melting at 136·5° is formed. This acid is also obtained by oxidising oleic acid with potassium permanganate (A. Saytzeff), whilst elaidic acid, on oxidation by permanganate, yields the dihydroxystearic acid melting at 99—100°. The latter acid is also formed by the action of potassium hydroxide on the chlorohydroxystearic acid obtained from oleic acid.

Similar isomerides are prepared by the action of potassium hydroxide solution on erucic and brassidic acids.

When the chlorohydroxybehenic acid, obtained from erucic acid, is treated with aqueous or alcoholic potash, the dihydroxybehenic acid is formed which melts at 99—100°; the latter acid is also a product of the oxidation of brassidic acid with potassium permanganate. The chlorohydroxybehenic acid from brassidic acid yields the dihydroxybehenic acid melting at 133°; and this acid is also prepared by the oxidation of erucic acid. By the action of potassium hydroxide on the additive compounds of hypochlorous acid with iso-oleic and iso-erucic acids, a dihydroxystearic acid corresponding with oleic acid is formed.
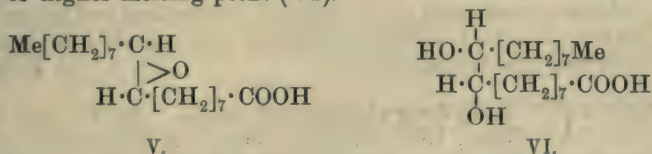
The formation of the dihydroxystearic acid of the lower melting point from oleic acid is represented as follows (I—III) :—

$$
\begin{array}{ccc}
& \overset{\textstyle Cl}{|} & & \overset{\textstyle H}{|} \\
Me[CH_2]_7 \cdot C \cdot H & & Cl \cdot C \cdot [CH_2]_7Me \\
H \cdot \underset{|}{C} \cdot [CH_2]_7 \cdot COOH & \longrightarrow & H \cdot \underset{|}{C} \cdot [CH_2]_7 \cdot COOH \\
OH & & OH \\
I & & II.
\end{array}
$$

$$
\begin{array}{ccc}
[\overset{\textstyle |}{C}H_2]_7Me & & \overset{\textstyle H}{|} \\
HO \cdot C \cdot H & & HO \cdot C \cdot [CH_2]_7Me \\
H \cdot \underset{|}{C} \cdot [CH_2]_7 \cdot COOH & \nearrow & H \cdot \underset{|}{C} \cdot [CH_2]_7 \cdot COOH \\
OH & & OH \\
III. & & IV.
\end{array}
$$
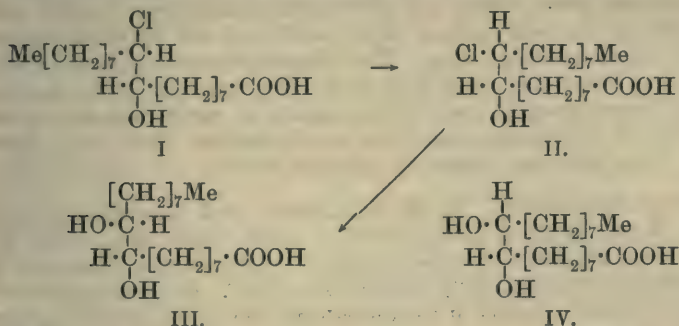
The dihydroxystearic acid of higher melting point (IV) is formed from elaidic acid in a similar way. The intramolecular change from (I) to (II) may either occur during the addition of hypochlorous acid, or during the action of the potassium hydroxide, but it cannot take place at a later stage, for the dihydroxystearic acid melting at 93–95°, prepared by oxidising elaidic acid, undergoes no change when treated with potassium hydroxide.

When oleic and erucic acids are heated with sulphurous anhydride or sodium hydrogen sulphite, 50 per cent. of the acids are converted into elaidic and brassidic acids respectively (*J. Russ. Chem. Soc.*, 24, 477), and elaidic acid, when similarly treated, yields oleic acid, only 20 per cent. of the acid, however, being attacked. In these reactions, sulpho-acids are probably intermediate products.

By the action of silver oxide on the chloro-, or, better, on the bromo-hydroxystearic acid prepared from oleic and elaidic acids, the dihydroxystearic acid of higher melting point is formed together with another compound not yet examined. The abnormal formation of this dihydroxy-acid is probably due to the high temperature of the reaction. When the chlorohydroxystearic acid obtained from oleic acid is converted into the monacetyl derivative of the dihydroxy-acid, and this then hydrolysed, the dihydroxystearic acid melting at 128—129° is formed, whilst from elaidic acid, under similar conditions, two dihydroxystearic acids are obtained, the one melting at 127—128° and the other at 93—95°. By the action of barium hydroxide on the chlorohydroxystearic acid prepared from elaidic acid, a glycidic acid (V) is formed which melts at 57—60°, and, when treated with potassium hydroxide or dilute sulphuric acid, yields the dihydroxystearic acid of higher melting point (VI).

$$
\begin{array}{ccc}
Me[CH_2]_7 \cdot C \cdot H & & \overset{\textstyle H}{|} \\
\quad \underset{|}{|}{>}O & & HO \cdot C \cdot [CH_2]_7Me \\
H \cdot C \cdot [CH_2]_7 \cdot COOH & & H \cdot \underset{|}{C} \cdot [CH_2]_7 \cdot COOH \\
& & OH \\
V. & & VI.
\end{array}
$$

The chlorohydroxystearic acid prepared from oleic acid, when treated

with barium hydroxide, yields glycidic acid in an uncrystallisable form, and this acid, when hydrolysed, forms the dihydroxystearic acid of lower melting point, whilst the chlorohydroxy-acid from iso-oleic acid forms the glycidic acid melting at 57—60°, and the dihydroxystearic acid of higher melting point. The chlorohydroxy-acid from elaidic acid is thus less stable than that from oleic acid, for it is changed into its stereoisomeride even by the action of weak reagents, whilst the action of sulphurous anhydride on elaidic and oleic acids shows that of these acids the former is the more stable.   E. W. W.

Elaidic Anhydride. By M. EMELJANOFF and ALEXIUS ALBITZKY (*Chem. Centr.*, 1899, i, 1070 ; from *J. Russ. Chem. Soc.*, 1899, **31**, 106—107).—Elaidic anhydride, prepared by the method described in a preceding abstract (p. 862), melts at 49—51·5°. By passing ammonia into the ethereal solution of the anhydride, the *amide*, which melts at 93—94°, is formed.   E. W. W.

Wood Oil. By MORIZ KITT (*Chem. Zeit.*, 1899, **23**, 23, 38).— This oil, which occurs to the extent of about 40 per cent. in the seeds of *Aleurites cordata* (belonging to the *Euphorbiaceæ*, and chiefly found in Japan), has been often the subject of investigation (compare Abstr., 1898, i, 628). The author's results are as follows : An oil, labelled " Yutshing," of a pale yellow colour, has a sp. gr. 0·9413 at 15° ; saponification number, 190·7—191·0 ; iodine number, 157·5—158·4 ; acidity, as oleic acid, 3·90 ; melting point of the fatty acids, 35—39·5° ; saponification number of the acids, 197·3—197·8 ; and yield of insoluble fatty acids about 82 per cent. Another oil, much darker in colour, and of greater viscosity, was also investigated ; the tabulated results do not greatly differ from the foregoing, the difference being most marked in the acidity number (6 95). This oil was reinvestigated after it had been solidified by exposure to light, and the results were practically the same. Wood oil has the remarkable property of gelatinising when heated to 282° ; it then is only partially soluble in benzene. The results obtained from this product, including the acetyl number, are given in tables.   L. DE K.

The Fatty Oil of Tropæolum Majus. By JOHANNES GADAMER (*Arch. Pharm.*, 1899, **237**, 471—474).—The oil extracted by ether from the pulverised seeds of *Tropæolum majus* consists largely of trierucin, $C_3H_5(C_{22}H_{41}O_2)_3$. When this glyceride is mixed with dilute nitric acid and is then treated with potassium nitrate, it is converted into tribrassidin, which melts at about 54° (not 47°).

When the oil is hydrolysed with caustic soda, phytosterol, equal in amount to 0·91 per cent. of the oil, resists hydrolysis. From the alkaline solution, erucic acid can be isolated ; nitric acid and potassium nitrite convert it into brassidic acid much more readily than they convert trierucin into tribrassidin.   C. F. B.

Vinylglycollic (α-Hydroxybutenoic) Acid. By G. VAN DER SLEEN (*Rec. Trav. Chim.*, 1899, **18**, 302—304).—A preliminary communication dealing with vinylglycollic acid, $CH_2:CH \cdot CH(OH) \cdot COOH$. When treated with caustic soda, this substance yields three crystalline

acids, one of which is probably identical with the propionylformic (α-ketobutenoic) acid, $CH_3 \cdot CH_2 \cdot CO \cdot COOH$, obtained as an oil by Claisen and Moritz (Trans., 1880, **37**, 691); the other products are being investigated. G. T. M.

Constitution of Inorganic Compounds. XIX. Oxalato-platinum Compounds. By ALFRED WERNER and E. GREBE (*Zeit. anorg. Chem.*, 1899, **21**, 377—388).—Sodium platino-oxalate, $Na_2Pt(C_2O_4)_2 + 4H_2O$, prepared by adding sodium hydroxide to the copper coloured sodium salt formed by the action of oxalic acid on sodium platinate until a yellow solution is obtained, crystallises in long, lemon-yellow prisms, and yields a bright red, crystalline magma when the hot solution is rapidly cooled; after a short time, the red salt changes into the yellow salt, and this change can be brought about many times with the same solution. The *calcium* salt, with $8H_2O$, obtained by adding calcium chloride to a saturated solution of the sodium salt, crystallises in orange-yellow prisms, and is easily soluble in water. It is converted into a red modification, with $4H_2O$, when heated with water on the water-bath; this crystallises in dark red leaflets, dissolves slowly in water, and then separates in the yellow modification.

Dichloroplatinioxalates.—The *sodium* salt, $Na_2Cl_2Pt(C_2O_4)_2 + 8H_2O$, is obtained by treating a hot solution of sodium platino-oxalate with chlorine until a bright yellow solution is obtained, and then, without stopping the current of chlorine, concentrating on the water-bath; it separates in large, bright yellow crystals, is very soluble in water, decomposes on exposure to the air, and slightly explodes when heated. The *potassium* salt, with $1H_2O$, obtained in the same manner as the sodium salt, to which it is very similar, separates in prismatic crystals. The *calcium* salt, with $6H_2O$, obtained both from the red or yellow modification of the preceding calcium salt by the action of chlorine, separates in beautiful, dark yellow crystals, and is very soluble in water.

Platiniplatino-oxalates.—The *sodium* salt, $Pt_5(C_2O_4)_{10}Na_8 + 20H_2O$, obtained by treating a hot solution of sodium platino-oxalate with a small quantity of chlorine, crystallises in small prisms, is bright brown in transmitted light, has a beautiful, copper-bronze lustre, is stable on exposure to the air, and explodes when heated. The *potassium* salt, with $12H_2O$, is similar to the sodium salt, but of a brighter colour. The *calcium* salt, prepared from the red calcium platino-oxalate, forms dark brownish-red crystals having a faint bronze lustre, is stable on exposure to the air, and explodes on heating. The *salt* obtained from the yellow calcium platino-oxalate crystallises in small, yellowish-brown prisms. The results of the analysis gave numbers which did not conform to any probable formula. E. C. R.

Formation of β-Bromalkylsuccinic Acids by Addition of Hydrogen Bromide to Homologues of Citraconic Acid. By W. SSEMENOFF (*Chem. Centr.*, 1899, i, 1070—1071; from *J. Russ. Chem. Soc.*, 1899, **31**, 115—135).—In unsaturated monobasic acids, the position of the double linking in regard to that of the carboxyl group determines also the position of the bromine atom in the additive compounds formed with hydrogen bromide, and in the case of unsaturated dibasic

acids, if the double linking is between the carboxyl groups, a β-compound is formed, and in other cases a γ-compound.

β-*Bromethylsuccinic acid*, $COOH \cdot CBrEt \cdot CH_2 \cdot COOH$, prepared by the action of hydrobromic acid of sp. gr. 1·49 on methylcitraconic anhydride at 0°, separates in monoclinic crystals, melts at 140—141°, is easily soluble in ether, hot water, or chloroform, and less so in cold water or benzene. A small quantity of a bye-product was also isolated. The α-compounds prepared by Bischoff (Abstr., 1891, **290**, 1221) melt at 111—116° and at 202·5° respectively. β-Bromethylsuccinic acid, when decomposed with a small excess of sodium carbonate, yields a-*ethylacrylic acid*, $CH_2 \dot{:} CEt \cdot COOH$, which boils at 179·5—180·5° under 760 mm. pressure, and has a sp. gr. 1·0106 at 0°/0°. The *calcium, barium*, and *silver* salts are described. When α-ethylacrylic acid is cooled and treated with $1\frac{1}{2}$ times the theoretical quantity of a 0·5 per cent. alkaline solution of potassium permanganate, it is instantly oxidised. The volatile portion of the product contains formic and propionic acids, whilst from the residue, a-*ethylglyceric acid*, $OH \cdot CH_2 \cdot CEt(OH) \cdot COOH$, may be isolated by means of its lead salt. This acid crystallises from ether in prisms, melts at 99—100°, is easily soluble in ether, and on further oxidation yields formic and propionic acids. The *lead* salt, $(C_5H_9O_4)_2Pb$, crystallises in square plates.

β-*Bromopropylsuccinic acid*, $COOH \cdot CPrBr \cdot CH_2 \cdot COOH$, prepared from ethylcitraconic anhydride, melts at 122—123°, and is soluble in water or chloroform. The aqueous solution appears to be supersaturated, and the peculiarity of the arrangement of the crystals which separate out from it is remarkable. When decomposed in alkaline solution, this acid forms a-*propylacrylic acid*, $CH_2 \dot{:} CPr \cdot COOH$, which boils at 199° under 745 mm. pressure and has a sp. gr. 0·9338 at 0°/0°. The *calcium, barium*, and *silver* salts are described. When α-propylacrylic acid is oxidised with potassium permanganate, a-*propylglyceric acid*, $OH \cdot CH_2 \cdot CPr(OH) \cdot COOH$, together with some formic and butyric acids, is formed. α-Propylglyceric acid melts at 94—95°, and is soluble in ether. The *lead* salt crystallises in square plates.

β-*Bromisopropylsuccinic acid* may be prepared in a similar way to the preceding acid, and good yields of the crude acid, which melts and decomposes at 152°, are obtained. By the action of water at 60—70°, it yields a volatile acid which has an extremely unpleasant odour. The crude acid, when treated with sodium carbonate, yields a-*isopropylacrylic acid*, $CH_2 \dot{:} CPr^\beta \cdot COOH$, which boils at 192·5—193°, has a sp. gr. 0·9854 at 0°/0°, and is slightly soluble in water. The *calcium* and *silver* salts are described. By oxidising with potassium permanganate, this acid yields a-*isopropylglyceric acid*, $OH \cdot CH_2 \cdot CPr(OH) \cdot COOH$, which melts at 102—103°, and is easily soluble in ether; some volatile acids are also formed. E. W. W.

Influence of Excess of Sodium Carbonate on the Decomposition of β-Bromalkylsuccinic Acids. By W. SSEMENOFF (*Chem. Centr.*, 1899, i, 1205; from *J. Russ. Chem. Soc.*, 1899, **31**, 283—296. Compare preceding abstract).—The non-volatile acids obtained by decomposing β-bromalkylsuccinic acids with sodium carbonate, are found to be β-hydroxyalkylsuccinic acids, and the quantity produced is proportional
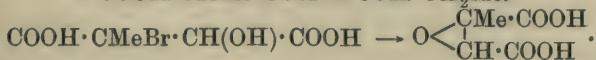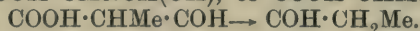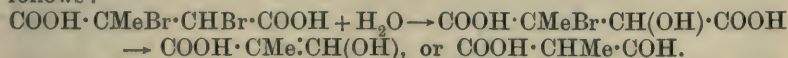
to the excess of sodium carbonate, this excess preventing the further decomposition of the acids. *β-Hydroxyethylsuccinic acid*,
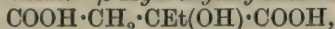
$$COOH \cdot CH_2 \cdot CEt(OH) \cdot COOH,$$

crystallises from alcohol in short prisms and melts at 131—133°. The *calcium* salt crystallises with $2H_2O$. *β-Hydroxypropylsuccinic acid*, $COOH \cdot CH_2 \cdot CPr^a(OH) \cdot COOH$, separates from ether in thread-like crystals and melts at 127—128°. *β-Hydroxyisopropylsuccinic acid*, $COOH \cdot CH_2 \cdot CPr^\beta(OH) \cdot COOH$, crystallises from ether in transparent, rectangular crystals and melts at 165—166°. Dimethylitaconic acid is also formed in the preparation of this acid, probably by the elimination of water. *Hydroxypyrotartaric acid* is also obtained, together with metacrylic acid, when β-bromopyrotartaric acid is treated with an excess of sodium carbonate. This acid melts at 115—117°, and is rather sparingly soluble in ether. Mesaconic acid could not be detected in the products of this reaction.

The influence of conditions in regard to time, amount of excess of sodium carbonate, and concentration, are discussed in the original paper. The decomposition of dibromohydratropic acid by sodium carbonate shows that the excess of carbonate has also an important effect in this case. E. W. W.

Influence of Excess of Sodium Carbonate on the Decomposition of Dibromocitrapyrotartaric Acid. By W. SSEMENOFF (*Chem. Centr.*, 1899, i, 1205—1206; from *J. Russ. Chem. Soc.*, 1899, **31**, 296—305).—When dibromocitrapyrotartaric acid is decomposed in alkaline solution, hydrogen bromide, carbonic anhydride, bromometacrylic acid, and propaldehyde are formed (Fittig), but in the presence of an excess of sodium carbonate (10 mols.) the decomposition is limited, and, in addition to hydrogen bromide, carbonic anhydride, acetaldehyde, and bromometacrylic acid, a considerable quantity of hydroxycitraconic acid is obtained. The mechanism of this reaction is discussed in detail in the original paper, and is assumed to be as follows :

$$COOH \cdot CMeBr \cdot CHBr \cdot COOH + H_2O \rightarrow COOH \cdot CMeBr \cdot CH(OH) \cdot COOH$$
$$\rightarrow COOH \cdot CMe\dot{:}CH(OH), \text{ or } COOH \cdot CHMe \cdot COH.$$
$$COOH \cdot CHMe \cdot COH \rightarrow COH \cdot CH_2Me.$$

$$COOH \cdot CMeBr \cdot CH(OH) \cdot COOH \rightarrow O \!\! <^{\dot{C}Me \cdot COOH}_{CH \cdot COOH} .$$

A similar decomposition occurs in the case of dibromohydratropic acid, a-hydroxy-β-bromohydratropic acid, $CH_2Br \cdot CPh(OH) \cdot COOH$, being first formed, and then decomposing into $CPh(OH)\!\!:\!\!CH_2 \rightarrow Ph \cdot COMe$, or $CH_2(OH) \cdot CPh(OH) \cdot COOH$, according to the amount of the excess of sodium carbonate. E. W. W.

Oxidation Products of Camphoric Acid. By LUIGI BALBIANO (*Real. Accad. dei Lincei*, 1899, **8**, 422—427. Compare Abstr., 1895, i, 552, 678; 1897, i, 253).—By reducing the acid of the composition $C_8H_{12}O_5$, which is the principal oxidation product of camphoric acid, $a\beta\beta$-trimethylglutaric acid and a lactonic acid are obtained; the author now shows the latter to be 3-dimethyl-4-methylpentane-2 : 5-olidoic acid, $CHMe \!\! <^{CO \cdot O}_{CMe_2} \!\! > CH \cdot COOH.$
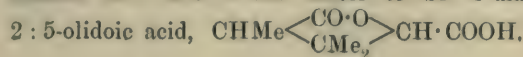
On heating the lactonic acid with hydriodic acid under pressure, it is converted into $\alpha\beta\beta$-trimethylglutaric acid.

2-*Bromo*-3-*dimethyl*-4-*methylpentane*-2 : 5-*olidoic acid*,

$$CHMe\begin{matrix}CO\cdot O\\CMe_2\end{matrix}\Big\rangle CBr\cdot COOH,$$
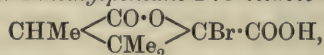
crystallises from benzene in groups of small, white, glistening prisms melting at $142-145°$; it is decomposed by water with formation of hydrogen bromide. When heated with alkalis or barium hydroxide, it is converted into oxalic acid and another dibasic acid which crystallises in beautiful, glassy plates melting at $67-69°$; it is either a hexamethyladipic acid, $C_{12}H_{22}O_4$, or a hexamethyltetramethylenedicarboxylic acid, $C_{12}H_{20}O_4$.

By acting on trimethylglutaric anhydride with bromine, *bromotrimethylglutaric anhydride* is obtained; when precipitated from a benzene solution by the gradual addition of light petroleum, it forms soft, white, sticky needles melting at $186-188°$. It is very soluble in benzene, and almost insoluble in light petroleum. By treating this bromanhydride with alcohol, diethylic bromotrimethylglutarate is obtained together with another ethylic salt which, on decomposition with sulphuric acid, yields 3-dimethyl-4-methylpentane-2 : 5-olidoic acid. This acid gives a *calcium* salt, $(C_8H_{11}O_4)_2Ca + 2H_2O$, which crystallises from water in small needles. The *lead* salt, $(C_8H_{11}O_4)_2Pb + 2H_2O$, crystallises in glistening, prismatic needles, soluble in water, and melting at $130-136°$; the anhydrous salt softens at $168°$, melts at $174°$, and on cooling solidifies to a transparent, glassy mass.

<div align="right">T. H. P.</div>

Action of Tartaric and Citric Acids on Metallic Iron. By KARL ULSCH (*Chem. Zeit.*, 1899, **23**, 658. Compare this vol., ii, 802). —Aqueous solutions of both citric and tartaric acids act slowly on iron, liberating hydrogen. As the reaction is so slow, the volume of hydrogen given off with a mixture of $N/10$ suphuric and $N/10$ tartaric acid was measured, a shaking apparatus being employed to accelerate the evolution of hydrogen. It was found that the amount evolved from the tartaric acid corresponded with the formation of the salt $Fe_2C_4H_2O_6$. Similarly, with citric acid, the amount of hydrogen agrees with the formation of the salt $Fe_2C_6H_4O_7$. In each case, therefore, not only the carboxylic hydrogen, but also the hydroxylic hydrogen had been replaced.

<div align="right">J. J. S.</div>

Alkali Copper Tartrates and Fehling's Solution. By FRIEDRICH BULLNHEIMER and E. SEITZ (*Ber.*, 1899, **32**, 2347—2352. Compare Masson and Steele, Trans., 1899, **75**, 725).—*Sodium copper ditartrate*, $C_4H_2O_6CuNa_2,C_4H_2O_6Na_4 + 13H_2O$, obtained by warming a mixture of tartaric acid, caustic soda, copper hydroxide, and water, filtering, shaking the filtrate with 96 per cent. alcohol, and allowing the lower layer which separates to crystallise in a desiccator, forms beautiful, light blue, deliquescent, monoclinic crystals, and dissolves in water with an alkaline reaction, is insoluble in alcohol, and is decomposed by heat. *Potassium copper ditartrate*, $C_4H_2O_6CuK_2,C_4H_2O_6K_4 + 8H_2O$, obtained similarly, forms harder crystals, and is darker in colour than the sodium compound.

On evaporating an aqueous solution of Rochelle salt, copper hydroxide, caustic potash, and caustic soda, two *sodium potassium copper ditartrates* separate; *one* of these, $C_8H_4O_{12}CuNa_4K_2 + 11H_2O$, closely resembles the sodium compound already described, whilst the other, $C_8H_4O_{12}CuK_3Na_3 + 11H_2O$, forms larger, monoclinic crystals of a deeper colour $[a : b : c = 1\cdot29 : 1 : 0\cdot84 ; \beta = 100° 30']$; the latter is more conveniently obtained by adding a mixture of methylic and ethylic alcohols to an aqueous solution of Rochelle salt, copper tartrate, caustic potash, and caustic soda.

Since 1 mol. of Rochelle salt in aqueous solution is capable of dissolving 1 mol. of copper hydroxide, it is usually assumed that there is present in Fehling's solution one or both of the compounds $C_4H_2O_6CuNa_2$ or $C_4H_2O_6CuKNa$; as, however, the *compound* $C_4H_2O_6CuNa_2 + 2H_2O$, which the authors have isolated by a method subsequently to be described, is decomposed on warming with water into copper oxide and sodium copper ditartrate, whereas Fehling's solution remains unchanged on heating, it is probable that the latter solution contains one or both of the ditartrates $C_8H_4O_{12}CuK_2Na_4 + 11H_2O$, or $C_8H_4O_{12}CuK_3Na_3 + 11H_2O$.

On dissolving copper tartrate in concentrated aqueous ammonia, adding alcohol, and cooling to 0°, dark blue crystals of *cupritetrammonium tartrate*, $C_4H_4O_6Cu(NH_3)_4 + 2H_2O$, separate; *copper cupritetrammonium tartrate*, $C_4H_2CuO_6Cu(NH_3)_4$, is obtained similarly from a solution of ammonium tartrate, copper hydroxide, and aqueous ammonia.   W. A. D.

Hydroxygluconic Acid. By Otto Ruff (*Ber.*, 1899, **32**, 2269—2273).—In the preparation of *d*-arabinose by the oxidation of calcium gluconate, the calcium and iron salts which remain after the separation of this substance show marked reducing properties, and contain appreciable quantities of calcium hydroxygluconate, which, owing to its insolubility, can be readily isolated. Hydroxygluconic acid, $OH\cdot CH_2\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot COOH$, is identical with the compound obtained by Boutroux (Abstr., 1890, 1399) by the bacterial fermentation of calcium gluconate, but differs from the hydroxygluconic acid described by W. Tiemann (*Zeit. Verein Rübenzuck-Ind.*, **40**, 787), as being formed when calcium gluconate is oxidised with bromine. The latter substance, however, seems to be gluconic acid containing a small quantity of hydroxyketonic acids; Tiemann's potassium salt was potassium gluconate and his osazone, *gluconic acid phenylhydrazide*, a substance separating from methylic alcohol in prisms and melting at 200°.   J. F. T.

Preparation of Monobasic Acids of the Sugar Group. By Otto Ruff (*Ber.*, 1899, **32**, 2273—2274).—The great drawback to Kiliani's process for the preparation of large quantities of monobasic acids of the sugar group is the loss of bromine which occurs during the reaction. The author finds that an equally good yield of these acids is obtained when only a little more than the theoretical quantity of bromine is used.   J. F. T.

Condensation of Glutaconic Acid. By Hans von Pechmann (*Ber.*, 1899, **32**, 2301).—When acted on by ethylic formate, two

molecules of ethylic glutaconate condense to form a *polymeric* etheric salt, which forms a thick oil and boils at 224° under 22 mm. pressure. The polymeric *acid*, $C_{10}H_{12}O_8$, crystallises in white prisms, and melts and decomposes at 207°.   T. M. L.

Action of Methylic Alcohol on Imides of Dibasic Acids. By SEBASTIAAN HOOGEWERFF and WILLEM ARNE VAN DORP (*Rec. Trav. Chim.*, 1899, **18**, 358—366. Compare Abstr., 1898, i, 589).—*Methylic succinamate*, $NH_2 \cdot CO \cdot C_2H_4 \cdot COOMe$, obtained by heating succinimide with 8 parts of methylic alcohol at 170° for 3 hours, crystallises from a mixture of acetone and ether in nacreous plates melting at 89—91°; it is readily soluble in water and the ordinary organic solvents; it may also be prepared by heating silver succinamate with methylic iodide.

Succinoparanitrobenzylimide, prepared by heating an alcoholic solution of succinimide, paranitrobenzylic chloride, and caustic soda, crystallises from alcohol in colourless plates and melts at 150—152°.

Methylic succinoparanitrobenzylamate,

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot CO \cdot C_2H_4 \cdot COOMe,$$
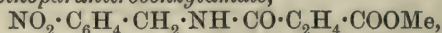
produced by heating the preceding compound with methylic alcohol at 170°, crystallises from benzene in colourless needles melting at 116—118·5°. When heated at 170° with excess of alcohol, this substance is partially reconverted into the imide; the reaction (imide+MeOH = methylic amido-ester) appears to be a reversible one. The methylic salts of maleamic, phthalophenylamic, and orthosulphamidobenzoic acids can also be prepared by heating the corresponding imides with methylic alcohol. *Methylic phthalamate*,

$$NH_2 \cdot CO \cdot C_6H_4 \cdot COOMe,$$
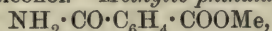
could not be obtained by this method, but is produced by heating silver phthalamate with methylic iodide dissolved in acetone; it melts at 98—102°, and when heated to 140° decomposes into phthalimide and methylic alcohol.   G. T. M.

Methyleneasparagine. By HUGO SCHIFF (*Chem. Zeit.*, 1899, **23**, 20—21).—*Methyleneasparagine*, $COOH \cdot CH(N:CH_2) \cdot CH_2 \cdot CO \cdot NH_2$, is obtained when the requisite quantity of asparagine is dissolved in slightly warm 20 per cent. formaldehyde solution and the syrupy product allowed to crystallise; it may also be obtained by cooling a solution of asparagine in hot water to 40—45° and then adding the requisite quantity of 40 per cent. formaldehyde. It crystallises in colourless plates or nodular masses, dissolves readily in warm water, and has a strong tendency to form supersaturated solutions; its aqueous solution has a decidedly acid reaction, is highly lævorotatory, and does not give the biuret reaction. The *copper* salt, $(C_5H_7O_3N_2)_2Cu + 5H_2O$, crystallises in dark blue needles; neither the acid nor its salts lose formaldehyde when exposed to the air.

Dimethyleneasparagine, probably identical with the compounds described by Goldschmidt (*Chem. Zeit.*, 1898, **22**, 374), is obtained when finely powdered asparagine (1 mol.) is dissolved in warm 25—30 per cent. formaldehyde (3 mols.). It forms a fine powder, and in a moist condition readily gives up formaldehyde when exposed to the air, the product left being methyleneasparagine. Two sparingly soluble *copper*

salts, $(C_6H_7N_2O_3)_2Cu + 1\frac{1}{2}H_2O$ and $C_5H_7N_2O_3 \cdot Cu \cdot C_6H_7N_2O_3 + H_2O$, have been prepared. J. J. S.

Alkyldiazourethanes (so-called Nitrosoalkylurethanes). By JULIUS W. BRÜHL (*Ber.*, 1899, **32**, 2177—2178).—Hantzsch (this vol., i, 686) assigns to nitrosourethane and its methyl derivative the diazo-formulæ $COOEt \cdot N \colon N \cdot OH$ and $COOEt \cdot N \colon N \cdot OMe$, and to the isomeride of the latter, which is obtained by the action of nitrous acid on methylurethane, the formula $COOEt \cdot NMe \cdot NO$. As regards the first point, the author some time ago (Abstr., 1897, i, 339) assigned the formula $COOEt \cdot N \colon N \cdot OEt$ to the ethyl derivative of nitrosourethane; he has also given reasons (Abstr., 1898, ii, 362) for assigning to the isomeride, not the constitution suggested by Hantzsch, but a diazo-structure, as expressed by the formula $COOEt \cdot NR {<}{\overset{N}{\underset{O}{|}}}$.

C. F. B.

Action of Argon and Nitrogen on Mercury Methyl and Mercury Phenyl. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, **129**, 378—379).—When a silent electric discharge is passed through argon in the presence of mercury dimethyl, the mercuric compound is decomposed, but argon is not absorbed and no luminosity is produced; if, however, mercury diphenyl is substituted for the mercury dimethyl, a green luminosity is produced, which, on account of the low vapour pressure of the mercuric compound, is not very intense. After the silent discharge has been acting for 41 hours, there is an absorption of argon equal to 8·9 per cent. of the gas taken. When a silent electric discharge is passed through nitrogen in the presence of mercury dimethyl, there is an absorption of nitrogen and the condensed substance has the composition $C_2H_{3\cdot 4}N_{0\cdot 50}$.

H. R. LE S.

Preparation of Organo-Zinc Compounds and Synthesis of Hexane. By L. SIMONOWITSCH (*Chem. Centr.*, 1899, i, 1066; from *J. Russ. Chem. Soc.*, 1899, **31**, 38—42).—A 92 per cent. yield of zinc ethyl is obtained by gradually heating a mixture of equal weights of dry ethylic iodide and zinc dust from 80° to 96°. Zinc dust is previously treated with acid and dried in carbonic anhydride at 160—180°, and zinc shavings are added to the mixture in quantity sufficient for a portion to project from the surface of the liquid. When all the ethylic iodide has disappeared, the product is distilled. The whole process requires only $1\frac{1}{2}$—2 hours. For the preparation of zinc methyl, Ipatieff's method (*J. Russ. Chem. Soc.*, **27**, 364) is recommended, zinc dust being used, however, instead of zinc shavings. By the action of isobutylic iodide on zinc ethyl iodide, ZnEtI, at 95°, ethylene, isobutylene, and a hexane boiling at 47·5—50°, and hence probably trimethylpropane, are formed. The sp. gr. of the last compound is 0·7305 at 0°. E. W. W.

Preparation of Zinc Methyl. By W. WOROBÉEFF (*Chem. Centr.*, 1899, i, 1067; from *J. Russ. Chem. Soc.*, 1899, **31**, 45—46).—When methylic iodide is heated with zinc dust and zinc shavings in an iron

vessel, the reaction takes place more quickly, but the yield of zinc methyl is reduced from 87 (Ipatieff, *J. Russ. Chem. Soc.*, **27**, 364) to 78 per cent. E. W. W.

Preparation of Zinc Isopropyl. By J. Bohm (*Chem. Centr.*, 1899, i, 1067 ; from *J. Russ. Chem. Soc.*, 1899, **31**, 46—47).—A 25 per cent. yield of zinc isopropyl which boils at 135° is obtained by Simonowitsch's method (preceding abstracts), the mixture being kept at 40°. The product decomposes when distilled, with evolution of gas and fumes of zinc oxide. E. W. W.

Acetylthiophenine [Acetamidothiophen]. By Enrico Rimini (*Chem. Zeit.*, 1899, **23**, 266).—Acetylthiophen ketoxime is readily converted by the Beckmann reaction into *acetamidothiophen*, $C_4H_3S\cdot NHAc$. The molecular rearrangement is best brought about by dissolving the oxime in dry ether, cooling with a freezing mixture, adding phosphorus pentachloride until the reaction ceases, washing the ethereal solution with water, and finally crystallising the product from alcohol. In appearance, it resembles acetanilide. J. J. S.

Trimethylene. By Marcellin P. E. Berthelot (*Compt. rend.*, 1899, **129**, 483—491).—The action of bromine on propylene in presence of water is much more rapid than on trimethylene, and affords a means of purifying the latter, which, however, is slowly affected, and if sufficient time is allowed, is also completely absorbed. The difference between the rates of action is sufficient to permit of the use of bromine for the approximate analysis of a mixture of the two gases.

When propylic or isopropylic alcohol is heated with zinc chloride, the product is mainly propylene mixed with small quantities of propane, hydrogen, and liquid hydrocarbons, but no trimethylene. Similar results are obtained with concentrated sulphuric acid.

Trimethylene, when heated with zinc chloride at its melting point, is gradually converted into propylene ; when heated alone, it is almost completely converted into propylene, mixed with some paraffins, ethylene, and hydrogen. Propylenic bromide is very rapidly attacked by zinc in presence of alcohol at the ordinary temperature, whereas a temperature of 60—70° is required in the case of trimethylenic bromide, the liberated trimethylene being partly converted into propylene.

These facts illustrate the relative instability of trimethylene, and are in accordance with thermochemical data. C. H. B.

Cyclic Acetone Bases. By Hermann Pauly (*Ber.*, 1899, **32**, 2244).—Triacetonamine is formed when diacetonamine oxalate is boiled with acetone, but this method is not suitable for its preparation. Guareschi's reaction, on the other hand, can not only be applied to the preparation of triacetonamine itself, but also to that of other acetone bases. Thus benzylidenemesityl oxide, $CHPh\colon CH\cdot CO\cdot CH\colon CMe_2$, is converted by aqueous ammonia into benzylidenediacetonamine, $CO{<}^{CH_2-CMe_2}_{CH_2\cdot CHPh}{>}NH.$ A. H.
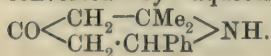
[Theory of] Unsaturated and Aromatic Compounds. By JULIUS W. BRÜHL (*Annalen*, 1899, **308**, 203—212. Compare Thiele, this vol., i, 554).—The author criticises Thiele's discussion of the constitution of unsaturated compounds and of benzene (*loc. cit.*), and fails to recognise an essential difference between his previously expressed views and those now put forward by Thiele.   M. O. F.

Constitution of Benzene. By JOHANNES THIELE (*Annalen*, 1899, **308**, 213—217. Compare this vol., i, 554).—A reply to the foregoing paper by Brühl.   M. O. F.

Nitrating Action of Nitric Acid on Saturated Hydrocarbons. VII. Nitration of Methylbenzenes. By MICHAËL I. KONOWALOFF (*Chem. Centr.*, 1899, i, 1237—1239; from *J. Russ. Chem. Soc.*, 1899, **31**, 254—273).—The results obtained by the action of nitric acid on toluene, meta- and para-xylene, mesitylene, and tertiary butyltoluene under different conditions are given in tables in the original paper. Toluene gives the best yield of nitro-derivatives containing the nitro-group in the side-chain, when heated with acid of sp. gr. 1·12 for 48 hours at 100° in a sealed tube. Metaxylene, paraxylene, and mesitylene may be nitrated by acid of sp. gr. 1·075, either in open or closed vessels, the first compound requiring the most time and mesitylene the least. The best yield of nitro-derivatives of butyltoluene is obtained by heating with acid of sp. gr. 1·075 at 105°. The nitro-compounds were purified by conversion into the sodium derivatives, and then decomposing these with carbonic anhydride or boric acid.

Phenylnitromethane [ω-nitrotoluene] boils at 141—142° under 35 mm. pressure, boils and decomposes at 225—227° under the ordinary pressure, has a sp. gr. 1·1756 at 0°/0°, 1·1598 at 20°/0°, and a specific refractive index $[n]_D$ 1·53230 at 20°. The alkali salts give the nitrolic acid reaction, yield isophenylnitromethane when treated with strong acids, and benzylamine when reduced with tin and hydrochloric acid. Metatoluenenitromethane [ω-nitrometaxylene], $C_6H_4Me \cdot CH_2 \cdot NO_2$, is a yellowish liquid which boils and decomposes at 140° under 35 mm. pressure, and has a sp. gr. 1·1370 at 0°/0° and 1·1197 at 20°/0°. By allowing it to remain with calcium chloride, metatoluic acid is formed. The potassium derivative of ω-nitrometaxylene crystallises in yellow leaflets. The sodium derivative is prepared by means of sodium ethoxide, and is a white powder. The calcium, barium, and strontium derivatives are white, stable powders. Metaxylylamine, $C_6H_4Me \cdot CH_2 \cdot NH_2$, boils at 205—205·5° under 750·5 mm. pressure, and has a sp. gr. 0·9809 at 0°/0° and 0·9654 at 20°/0°. The hydrochloride forms small crystals and melts and decomposes at 181—191°. The sulphate crystallises in large plates and melts at 250°. The platinochloride is insoluble in alcohol or ether, and melts at 198—200°; the aurichloride crystallises in leaflets containing $1H_2O$, and is soluble in water. *Paratoluenenitromethane* [ω-*nitroparaxylene*] melts at ¡11—12°, has a sp. gr. 1·1234 at 20°/0°, specific refractive index $[n]_D$ = 1·53106 at 20°, boils with slight decomposition at 150—151° under 35 mm. pressure, gives the nitrolic acid reaction in alkaline solutions, and decomposes into paratoluic acid. Several metallic derivatives are described. Paraxylylamine melts at

12·6—13·2°, boils at 204° under 739 mm. pressure, has a sp. gr. 0·9520 at 20°/0°, 0·9501 at 30°/0°, a specific refractive index 1·53639 at 20°, and rapidly absorbs carbonic anhydride from the air. *Metaxylene-metanitromethane* [ω-*nitromesitylene*], $C_6H_3Me_2 \cdot CH_2 \cdot NO_2$ [$Me_2:CH_2 \cdot NO_2$ = 1 : 3 : 5], crystallises in large plates, melts at 46—47°, boils and decomposes at 120—170° under 25 mm. pressure, forming mesitylenic acid and mesitylaldehyde, and other compounds. The alkali derivatives are soluble in water or alcohol, give the nitrolic acid reaction, are precipitated by metallic salts, and when treated with nitric acid of sp. gr. 1·155 yield mesitylenic acid. ω-Mesitylamine, $C_6H_3Me_2 \cdot CH_2 \cdot NH_2$ [$Me_2 : CH_2NH_2$ = 1 : 3 : 5], boils at 220—221° under 758 mm. pressure, has a sp. gr. 0·9631 at 0°/0°, 0·9500 at 20·5°/0°, specific refractive index 1·53046 at 20·5°, absorbs carbonic anhydride from the air with avidity, and is identical with Landau's compound (Abstr., 1893, i, 32). The hydrochloride crystallises in prisms, melts at 245—246°; the nitrate forms prisms and melts at 170°. 1-*Nitromethyl-2-nitro-3*:5-*dimethylbenzene* [ω : 2-*dinitromesitylene*], $NO_2 \cdot CH_2 \cdot C_6HMe_2(NO_2)_2$, prepared by further nitrating ω-nitromesitylene at −10° with nitric acid of sp. gr. 1·48, melts at 85·5—86°. The alkali salts are easily soluble in water, forming orange-red solutions, from which carbonic anhydride precipitates the original substance, and dilute sulphuric acid the isodinitro-compound. ω : 2-Dinitromesitylene, when oxidised by a 4 per cent. solution of potassium permanganate, yields orthonitromesitylenic acid, which melts at 210—212°. By the action of nitric acid of sp. gr. 1·51 on the original mononitro-compound or on the dinitro-compound, a mixture of crystalline compounds is formed, from which a *trinitro*-derivative, $C_9H_9(NO_2)_3$, may be isolated. This substance melts at 117·5—118·5°, is easily soluble in benzene, ether, or chloroform, and yields alkali salts, from which, by the action of carbonic anhydride, or of dilute sulphuric acid, the original compound is regenerated; an isonitro-compound could not be obtained.

The heats of combustion per gram-molecule and the melting points of the following isomeric nitromesitylenes are quoted :

	Melting point.	Heat of combustion.
$C_6H_2Me_3(NO_2)$	44°	1,216,660 Cal.
$C_6H_3Me_2 \cdot CH_2 \cdot NO_2$	46—47°	1,206,332 „
$C_6HMe_3(NO_2)_2$	86—87°	1,186,710 „
$C_6H_2Me_2(NO_2) \cdot CH_2 \cdot NO_2$ [= 1 : 3 : 4 : 5]	85·5—86°	1,165,857 „

In each case, the heat of combustion of the derivative containing the nitro-group in the side-chain is less than that of its isomeride containing this group in the benzene ring.   E. W. W.

Simple Method of Etherification of Phenols and Aldehydes by means of an Acid Radicle and Quick Method of Acetylation of Aromatic Amines containing Negative Groups. By GEORGES FREYSS (*Chem. Centr.*, 1899, i, 835—836 ; from *Bull. Soc. ind. Mulhouse*, 1899, 44—48).—Valeraldehyde is only attacked by acetic anhydride when it is heated with it under pressure at a high temperature, but when a drop of concentrated sulphuric acid is added to the mixture,

an energetic reaction takes place at the ordinary temperature; in like manner, a good yield of acetyl derivatives of many aldehydes, hydroxyaldehydes, phenols, substituted phenols containing negative groups, and polyhydric alcohols may be obtained. Amines containing one or more negative groups, amidophenols, &c., also yield large quantities of acetyl derivatives, but the preparation of mixed ketones from ethers of phenols, or of the hydrocarbons, C_nH_{2n-6}, by means of acetic anhydride and sulphuric acid is less satisfactory. Acetates were prepared in this way from phenol, guaiacol (the acetate is a liquid with a strong aromatic odour boiling at 239—241° under 738 mm. pressure), eugenol (the acetate is a liquid boiling at 278—279° under 750 mm. pressure), and orthonitrophenol. Diacetates from resorcinol, benzaldehyde, and parachlorometanitrobenzaldehyde (the salt forms yellowish, lustrous crystals melting at 97°), and mono- and tri-acetates from salicylaldehyde and of vanillin have also been prepared.   E. W. W.

Reactions of Phenylic Chlorocarbonates. By ALBERT MOREL (*Bull. Soc. Chim.*, 1899, [iii], 21, 815—823, 823—830. Compare this vol., i, 586, 747).—The phenylic chlorocarbonates are decomposed by water, very slowly at the ordinary temperature, but immediately at 100°, with formation of normal phenylic carbonates and the products of decomposition of carbonyl chloride. Similar decompositions are effected by the action of aqueous alkalis and solutions of basic lead acetate, silver nitrate, &c. With alkali alkyloxides, a mixture of normal phenylic and alkylic carbonates is obtained. Aliphatic alcohols have little or no action on phenylic chlorocarbonates in the cold, even in the presence of aluminium chloride, but on heating, the theoretical amount of hydrogen chloride is evolved, and excellent yields of mixed phenylic alkylic carbonates are obtained. The temperature required to bring about this reaction depends on the molecular weight and the constitution of the alcohol employed, and has been experimentally determined in the case of methylic (66°), ethylic (78°), normal and propylic (90°), butylic (103°), heptylic (142°), octylic (155°), and benzylic (160°) alcohols, and also for isopropylic (86°), isobutylic (99°), ordinary amylic (111°), and allylic (92°) alcohols. Better yields are obtained with alcohols requiring high than with those requiring low temperatures. The following compounds have been prepared by the method described.

Phenylic butylic carbonate is a colourless liquid boiling at 129—130° under 25 mm. pressure, has a sp. gr. 1·0507 at 0°, and a refractive index 1·47951 at 16·1°. *Phenylic heptylic carbonate* is a colourless liquid which boils at 136° under 25 mm. pressure, and has a sp. gr. 1·0465 at 0° and refractive index 1·47812 at 16·1°. *Phenylic octylic carbonate* is a colourless liquid boiling at 145° under 30 mm. pressure; it has a sp. gr. 1·0432 at 0°, and a refractive index 1·47647 at 16·1°. *Phenylic caprylic carbonate* is a colourless liquid boiling at 142—145° under 30 mm. pressure, has a sp. gr. 1·0492 at 0°, and a refractive index 1·48224 at 15·7°. *Phenylic benzylic carbonate* is a faintly yellow liquid which boils at 180—190° under 30 mm. pressure, has a sp. gr. 1·1366 at 0°, and a refractive index 1·49141 at 15·7°.

Orthotolylic ethylic carbonate, a colourless liquid, boils at 132° under

30 mm. pressure, has a sp. gr. 1·1271 at 0°, and a refractve index 1·49399 at 15·7°. Metatolylic ethylic carbonate is a colourless liquid boiling at 135—138° under 30 mm. pressure; it has a sp. gr. 1·1351 at 0° and a refractive index 1·49522 at 15·7°. Paratolylic ethylic carbonate is a colourless liquid which boils at 138—140° under 30 mm. pressure, has a sp. gr. 1·1389 at 0°, and a refractive index 1·49647 at 15·7°. This and the two preceding compounds are identical with those which Bender obtained by the action of ethylic chlorocarbonate on the three sodium tolyloxides.

Parachlorophenylic ethylic carbonate is a colourless liquid which boils at 135—145° under 30 mm. pressure, has a sp. gr. 1·1726 at 0°, and a refractive index 1·51700 at 15·7°.

Thymylic ethylic carbonate, a colourless liquid which boils at 145—154° under 25 mm. pressure, has a sp. gr. 1·1524 at 0°, and a refractive index 1·49981 at 15·7°; it has been prepared by Richter by treating ethylic chlorocarbonate with sodium thymyloxide.

The specific gravity of the mixed phenylic alkylic carbonates decreases as the molecular weight increases, at least for the series of normal alcohols, and the following measurements, together with those already quoted, show that a similar relation holds good for the indices of refraction. The numbers refer to the D-line at 15·7—16·1°; air temperature = 20°. Phenylic methylic carbonate, 1·50221; phenylic ethylic carbonate, 1·49093; phenylic propylic carbonate, 1·48640; phenylic isopropylic carbonate, 1·48429; phenylic isobutylic carbonate, 1·47334; phenylic isoamylic carbonate, 1·47768; phenylic allylic carbonate, 1·50258; guaiacylic methylic carbonate, 1·51736; guaiacylic ethylic carbonate, 1·50297; guaiacylic propylic carbonate, 1·49872; guaiacylic isobutylic carbonate, 1·46781; guaiacylic isoamylic carbonate, 1·47087; guaiacylic benzylic carbonate, 1·49265.

The second paper deals with the action of phenylic chlorocarbonates on phenols and on organic bases. Phenylic chlorocarbonates have no action on phenols in the cold, even in the presence of aluminium chloride, and, on heating, the only reaction which occurs is the decomposition of the chlorocarbonate with the formation of carbonyl chloride and normal phenylic carbonate. A similar decomposition takes place with anhydrous alkali phenyloxides, but by gradually adding a concentrated solution of the phenol in aqueous soda to a solution of the chlorocarbonate in benzene or ether, mixed phenylic carbonates are readily obtained. *Phenylic paratolylic carbonate,* prepared in this way from phenylic chlorocarbonate and sodium tolyloxide, crystallises in slender, colourless needles melting at 94°. *Phenylic guaiacylic carbonate* melts at 82°, *phenylic parachlorophenylic carbonate* at 92°, *guaiacylic parachlorophenylic carbonate* at 98°, and *guaiacylic paracresylic carbonate* at 99°.

Phenylic chlorocarbonates interact readily with ammonia in alcoholic solution, and phenylic, guaiacylic, tolylic, thymylic, and parachlorophenylic carbamates, all of which have been obtained by other methods and previously described, were prepared in this way. The following substituted carbamates were obtained in a similar manner by the action of primary and secondary amines. Phenylic phenylcarbamate, which Hofmann obtained by heating phenylic cyanate with phenol, crystallises

in slender, colourless needles melting at 125·5°. *Guaiacylic phenyl-carbamate* crystallises in slender, colourless needles, and melts at 136°. *Phenylic phenylcarbazinate,* from phenylhydrazine and phenylic chlorocarbonate, crystallises in small needles melting at 122—123°, decomposes at 200°, and has strong reducing properties. All these compounds are insoluble in cold, and almost insoluble in hot, water, but soluble in all organic solvents. They crystallise well from chloroform, and are insoluble in dilute acids. *Phenylic dipropylcarbamate* is a liquid which boils at 168° under 30 mm. pressure.

When phenylic chlorocarbonate and pyridine are mixed in alcoholic or ethereal solution, considerable heat is developed, probably due to the formation of an unstable additive product which decomposes into normal phenylic carbonate and a compound of pyridine with carbonyl chloride. The latter compound, which is also obtained as a yellowish-white precipitate by the direct action of pyridine on carbonyl chloride in toluene solution, appears to have the composition $COCl_2(C_5H_5N)_2$, and is very unstable. N. L.

Constitution of Dichlororthocresol. By C. MARTINI (*Gazzetta,* 1899, **29**, ii, 60—64).—The dichlororthocresol obtained by the action of sulphuryl chloride (2 mols.) on orthocresol (1 mol.) is identical with the compound melting at 55° prepared by Claus and Riemann (Abstr., 1883, 1111) by the direct action of chlorine.

Dichlororthomethoxytoluene, $C_6Cl_2H_2Me \cdot OMe$, obtained by the action of potassium hydroxide and methylic iodide on dichlororthocresol, melts at 29—30°, and on cooling remains liquid (even if shaken) until a temperature of 17° is reached, when it suddenly solidifies to a radiating mass of long prisms resembling menthol. It has an aromatic odour, and is very soluble in ether, alcohol, benzene, or light petroleum, its solutions exhibiting supersaturation. On oxidation with nitric acid, it yields the methylic derivative of dichlorosalicylic acid (*dichlorortho-methoxybenzoic acid*), $OMe \cdot C_6H_2Cl_2 \cdot COOH$, which crystallises from dilute alcohol in long, white, prismatic needles, sublimes with partial decomposition, and melts at 165·5—167°. The dichlorosalicylic acid obtained by the action of hydriodic acid on this compound melts at 219·5°, and is found to be identical with the 3 : 5-dichlorosalicylic acid described by Lössner and by Smith as melting at 214°, and by Zincke as melting at 219°.

It is concluded that the dichlororthocresol melting at 55° has the constitution [Me : OH : Cl : Cl = 1 : 2 : 3 : 5]. T. H. P.

Constitution of Dichloroparacresol. By V. BERTOZZI (*Gazzetta,* 1899, **29**, ii, 35—41).—*Dichloroparamethoxytoluene,* $C_6H_2Cl_2Me \cdot OMe$, obtained by the action of methylic iodide and a methylic alcohol solution of potassium hydroxide on dichloroparacresol, is a colourless oil boiling at 234°. On oxidation with nitric acid, it yields dichloranisic acid, which crystallises from alcohol in large, white, shining needles melting at 200—201°, and is identical with the acid obtained by Reinecke by treating anisic acid with hydrochloric acid and potassium chlorate ; Reinecke gave the melting point 196°. With hydriodic acid, dichloranisic acid yields an acid forming small, acicular crystals melting at 265°, which proves to be identical with dichlorohydroxybenzoic acid

[Cl : Cl : OH : COOH = 3 : 5 : 4 : 1], the melting point of which was given by Lössner as 255—256°, and by Zincke as 259—260°.

Benzoyldichloroparacresol, $C_6H_2Cl_2Me \cdot OBz$, crystallises from light petroleum in large, monoclinic prisms melting at 89°.

It is concluded that dichloroparacresol has the constitution [Me : Cl : Cl : OH = 1 : 3 : 5 : 4]. T. H. P.

Action of Ether and Aluminium Chloride on Aromatic Hydrocarbons. By PAUL JANNASCH and A. RATHJEN (*Ber.*, 1899, **32**, 2391—2394. Compare Abstr., 1898, i, 565).—*Diethylphenol*, $C_6H_3Et_2 \cdot OH$ [?1 : 3 : 5], is made by heating phenol, ethylic ether, and aluminium chloride at 145°. It has a characteristic phenolic odour, dissolves sparingly in water but readily in alcohol, ether, benzene, or chloroform, crystallises from light petroleum in long, shining needles or large, compact prisms, melts at 77°, and boils at 239°. It dissolves readily in dilute soda and is reprecipitated by carbonic anhydride; its dilute alcoholic solution gives no coloration with ferric chloride. *Tribromodiethylphenol*, $C_6Et_2Br_3 \cdot OH$, separates from acetic acid in silky needles melting at 128°. *Trinitrodiethylphenol*, $C_6Et_2(NO_2)_3 \cdot OH$, separates from light petroleum in yellow leaflets or in magnificent, transparent rhombohedra, melts at 91°, is sparingly soluble in water, and dissolves readily in alcohol, ether, or benzene; with aniline, it gives a compound crystallising in golden-yellow needles.

Tetrethylphenol, $C_6HEt_4 \cdot OH$, formed when more ether and aluminium chloride is used than in the foregoing case, is very readily soluble in the usual media with the exception of water; it is obtained in long needles by leading hydrogen chloride in the alcoholic solution. It melts at 45° and boils at 270—271°.

Hydroxydiethylbenzaldehyde, $OH \cdot C_6H_2Et_2 \cdot CHO$, prepared from diethylphenol by the Gattermann reaction, is less readily soluble than diethylphenol in most media, and crystallises from boiling light petroleum in slender needles melting at 107°. The production of this aldehyde indicates that in diethylphenol the para-position is occupied by hydrogen, and the authors suggest that the compound has the constitution [CHO : Et$_2$: OH = 1 : 2 : 6 : 4].

The foregoing method of ethylation is regarded as a valuable one, the yield of product being usually very high. A. L.

Electrolytic Conductivity of Hydroresorcinols and δ-Ketonic Acids. By RUDOLF VON SCHILLING and DANIEL VORLÄNDER (*Annalen*, 1899, **308**, 184—202).—The acidic properties of hydroresorcinols are as strongly marked as those of δ-ketonic acids, although the carboxyl group is absent. The structural difference between the two classes of compounds does not amount to much more than ring-formation, as may be seen by comparing hydroresorcinol, $CH_2 \!\! <^{CH_2 \, - \, CO}_{CH_2 \cdot C(OH)} \!\! > CH$, with

γ-acetobutyric acid, $CH_2 \!\! <^{CH_2 \, - \, CO}_{CH_2 \cdot COOH} \!\! CH_3$, and cyclic, organic substances containing oxygen usually exhibit acidic properties more pronounced than those open-chain compounds of similar constitution; for instance, hydroresorcinol may be titrated with caustic alkali and phenolphthalein, whilst acetylacetone, $CH_3 \cdot CO \cdot CH:C(OH) \cdot CH_3$, gives no

definite end-point, and comparison of the first-named substance with ethylic β-ketohexamethylenecarboxylate, $CH_2 \begin{smallmatrix} CH_2——CH_2 \\ CH_2 \cdot C(OH) \end{smallmatrix} C \cdot COOEt$, indicates that the acidic influence of the carbonyl group of the ring is more powerful than that of the carbonyl radicle.

The authors have determined the electrolytic conductivity of certain hydroresorcinol derivatives and δ-ketonic acids, in order to ascertain which group of compounds is the more powerfully acidic. The results are summarised in the following table:

δ-Ketonic acids.	K.	Hydroresorcinol derivatives.	K.
γ-Acetobutyric	0·0022	Hydroresorcinol	0·00055
β-Methyl-γ-acetobutyric	0·0027	Methylhydroresorcinol	0·00057
β-Phenyl-γ-acetobutyric	0·0032	Dimethylhydroresorcinol	0·00071
β-Phenyl-γ-trimethacetobutyric	0·0025	Phenylhydroresorcinol	0·0012
		Furylhydroresorcinol............	0·0015
		Ethylic methylhydroresorcyl-	
		ate	0·0037
		Methylic dimethylhydroresor-	
		cylate	0·0048
		Ethylic phenylhydroresorcyl-	
		ate	0·0061
		Phenylhydroresorcylic nitrile.	0·0019
		Phenylmethylhydroresorcylic	
		nitrile	0·020

From this it appears that the δ-ketonic acids are 3—5 times stronger than the corresponding hydroresorcinols, and it becomes possible to distinguish these groups by conductivity determinations. The δ-ketonic acids cannot, however, be distinguished from the hydroresorcylic esters and nitriles by this means.

Conversion into a cyclic compound increases the acidity of acetyl-acetone ($K = 0·000005$) nearly 100 times. M. O. F.

Organic Syntheses by means of Ferric Chloride. By MARCELLUS NENCKI (*Ber.*, 1899, **32**, 2414—2419. Compare Abstr., 1897, i, 520).—From the behaviour of a mixture of benzene and benzoic chloride towards ferric chloride, it is found that syntheses by means of this agent are to be explained on the same principle as those effected by the agency of aluminium chloride. The *compound*, $(COPh_2, FeCl_3)_2, COPhCl, FeCl_3$, prepared by adding sublimed ferric chloride to a mixture of benzene and benzoic chloride, forms yellowish-brown, hygroscopic crystals readily soluble in alcohol or ether, but insoluble in petroleum; water eliminates ferric chloride, and gives rise to benzophenone and benzoic acid (compare Morrell and Crofts, Trans., 1898, **73**, 347).

Diacetylphloroglucinol, $C_6HAc_2(OH)_3$, prepared by heating phloroglucinol with acetic chloride and ferric chloride on the water-bath, and hydrolysing the ether thus produced, crystallises from water in pale yellow needles; it combines with 2 mols. of phenylhydrazine and hydroxylamine, forming pyrazoline and isoxazole derivatives respectively.

Syntheses by means of ferric chloride are sometimes attended by oxidising action. Chloroform and benzene, for instance, give rise to triphenylcarbinol, together with triphenylmethane, whilst acetic

chloride and metaxylene yield orthoparaxylic acid along with di-methylacetophenone; dibutylquinone is obtained instead of dibutyl-quinol from butylic chloride and quinol.   M. O. F.

Syntheses of Organic Compounds by means of Ferric Chloride. By N. MEISSEL (*Ber.*, 1899, **32**, 2419—2423. Compare foregoing abstract, and Abstr., 1897, i, 521).—Syntheses of dimethyl-acetophenone, dimethylbenzophenone, cymeneacetophenone, and ter-tiary butylmethylacetophenone have been effected by the agency of ferric chloride; the last named ketone, prepared from tertiary para-butyltoluene and acetic chloride, boils at 240—245°, and has a sp. gr. 0·9541 at 15°.

Triphenylmethane, triphenylcarbinol, and a small quantity of benz-aldehyde are obtained by the action of ferric chloride on chloroform and benzene. Para-isoamylphenol, $C_5H_{11} \cdot C_6H_4 \cdot OH$, prepared from isoamylic chlorocarbonate, phenol, and ferric chloride, was obtained by Liebmann on heating phenol with isoamylic alcohol and zinc chloride at 180°; it crystallises from petroleum, and melts at 93—94°. Parethylphenol is formed in the same way.   M. O. F.

Action of Tertiary Butylic Chloride on Dihydric Phenols in presence of Ferric Chloride. By A. GUREWITSCH (*Ber.*, 1899, **32**, 2424—2428. Compare the foregoing abstracts).—*Dibutylresorcinol*, $C_6H_2Bu_2(OH)_2$, crystallises in small plates containing $2H_2O$, and melts at 116—118°; the *diacetyl* derivative melts at 138°. The *butylic ether* of dibutylresorcinol, prepared by heating resorcinol with tertiary butylic chloride and ferric chloride, crystallises from dilute alcohol in white scales, and melts at 99°; aluminium chloride differs from ferric chloride in giving rise to dibutylresorcinol instead of the butylic ether. A mixture of concentrated nitric and sulphuric acids converts dibutylresorcinol into trinitroresorcinol, which melts at 175·5°.

Diamylresorcinol, $C_6H_2(C_5H_{11})_2(OH)_2$, obtained from resorcinol, tertiary amylic chloride, and ferric chloride, crystallises from dilute alcohol in needles and melts at 67°; the *diacetyl* derivative melts at 87—88°.

Dibutylcatechol, $C_6H_2Bu_2(OH)_2$, prepared from catechol, tertiary butylic chloride, and ferric chloride, crystallises from benzene in golden-yellow needles and melts at 85—86°.

Dibutylquinone, $C_6H_2Bu_2O_2$, produced on agitating quinol, tertiary butylic chloride and ferric chloride during 10 minutes at ordinary temperatures and pouring the liquid into water, crystallises from dilute alcohol, and melts at 150—151°; the *phenylhydrazone* crystallises from benzene and melts at 212°.

Butylphenol and para-amylphenol have been prepared by similar methods.   M. O. F.

Tertiary Dibutylpyrogallol. By L. RÓŻYCKI (*Ber.*, 1899, **32**, 2428—2429. Compare foregoing abstracts).—*Dibutylpyrogallol*, $C_6HBu_2(OH)_3$, prepared by heating pyrogallol with tertiary butylic chloride and ferric chloride, crystallises from petroleum in snow-white needles and melts at 119°; the *triacetyl* derivative melts at 163°.
                                                        M. O. F.

Retardation of Chemical Reactions due to Stereochemical Causes. By MAX SCHOLTZ (*Ber.*, 1899, **32**, 2251—2256).—It has been previously shown (Abstr., 1898, i, 305, 383, 565 ; and this vol., i, 541) that pentacyclic compounds are formed by the action of $a\delta$-dibromides on primary aromatic amines, unless other groups are in ortho-positions relatively to the amido-group, and that in such cases derivatives of $a\delta$-diamido-compounds are formed. The research has been extended by studying the action of trimethylenic bromide on aromatic amines, and somewhat similar results have been obtained, although there is not the same tendency to form a tetracyclic nitrogen system as there is to form a pentacyclic compound. Diphenyltrimethylenediamine, N-phenyltrimethyleneimine, and diphenyl-bistrimethylenedi-imine are all formed by the action of trimethylenic bromide on aniline. Diphenyltrimethylenediamine is a yellow, viscid liquid, and distils at 280—285° under 16 mm. pressure (compare Hanssen, Abstr., 1877, 577) ; it combines with either one or two equivalents of acid. The sulphate, $C_{15}H_{18}N_2,H_2SO_4$, melting at 156°, *hydrochloride* melting at 145°, and *platinochloride* have all been prepared.

N-phenyltrimethyleneimine, $CH_2 \begin{matrix} CH_2 \\ CH_2 \end{matrix} NPh$, obtained by repeated fractional distillation of the first fractions from the diamine, is a colourless, limpid oil distilling at 130—132° under 16 mm., and at 242—245° under atmospheric pressure. Its *picrate*, $C_9H_{11}N,C_6H_3N_3O_7$, crystallises in needles, and is readily soluble in alcohol. The third product, which is contained in the higher fractions, has not been obtained in a pure form.

Diorthotolyltrimethylenediamine, $CH_2(CH_2 \cdot NH \cdot C_6H_4Me)_2$, is the only condensation product obtained by heating an alcoholic solution of orthotoluidine (4 mols.) and trimethylenic bromide (1 mol.) for several hours on the water-bath ; it is separated from orthotoluidine hydrobromide by extraction with ether, and forms a yellowish oil distilling at 275—280° under 16 mm. pressure ; its *sulphate* melts at 216°.

Diphenylhexahydropyrimidine, $CH_2 \begin{matrix} CH_2 \cdot NPh \\ CH_2 \cdot NPh \end{matrix} CH_2$, is obtained as a crystalline deposit when diphenyltrimethylenediamine is well shaken with 40 per cent. formaldehyde solution at 40—50° ; it crystallises from alcohol in colourless prisms melting at 87°. Neither diorthoditolyltrimethylenediamine nor the corresponding para-compound (Bischoff, this vol., i, 280) is capable of undergoing condensation with formaldehyde. A toluene solution of diparatolyltrimethylenediamine reacts with a solution of carbonyl chloride in the same solvent, yielding the *chloride*, $CH_2[CH_2 \cdot N(COCl) \cdot C_6H_4Me]_2$, which crystallises in colourless prisms melting at 82°. J. J. S.

Action of Acid Chlorides on Benzylideneaniline. By KARL GARZAROLLI-THURNLACKH (*Ber.*, 1899, **32**, 2277—2279).—Molecular proportions of acetic or benzoic chloride react with benzylideneaniline at the ordinary temperature to form yellow, crystalline additive products of the formula $COR \cdot NPh \cdot CHPhCl$, which are difficult to purify and easily decomposed. The constitution is deduced from the fact that on boiling with alcohol they are decomposed into benzaldehyde,

hydrogen chloride and acetanilide or phenylbenzamide, according to the acid chloride used.   J. F. T.

Resolution of Isodiphenylhydroxyethylamine into its Optically Active Components. By EMIL ERLENMEYER, jun. (*Ber.*, 1899, **32**, 2377—2378).—On adding *d*-tartaric acid to a solution of isodiphenylhydroxyethylamine (this vol., i, 760) in absolute alcohol, the *tartrate* of the lævo-modification of the base separates nearly quantitatively in long needles; it melts at 176—177°, and in aqueous solution has $[a]_D - 37\cdot57°$, whilst the *base* melts at 113—114°, and has $[a]_D - 109\cdot66°$ in alcoholic solution. The *tartrate* of the dextro-modification is very soluble in alcohol, melts at 133—134°, and in aqueous solution has $[a]_D + 54\cdot33°$; the *dextro-base* melts at 112—113°, and has a specific rotatory power equal in magnitude to that of the lævo-modification,   W. A. D.

Paratolylpseudoazimidonitrobenzene, Picryl, and 2:4-Dinitrophenylmetaxylylhydrazine, and their Derivatives. By CONRAD WILLGERODT and HERMANN KLEIN (*J. pr. Chem.*, 1899, [ii], **60**, 97—112).—Paratolylpseudoazimidonitrobenzene,

$$C_6H_4Me\cdot N\!\!<\!\!^N_N\!\!>\!\!C_6H_3\cdot NO_2 \ [N:N:NO_2 = 1:2:4],$$
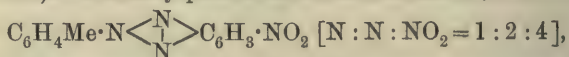
is best prepared by the action of sodium hydrogen carbonate on an alcoholic solution of tolylhydrazine and α-chlorodinitrobenzene. When reduced with stannous chloride, it gives the corresponding *amine*, which melts at 212—213° and crystallises from alcohol in yellow flakes, but on one occasion separated in pale green, silky needles having the same melting point; it dissolves slightly in ethylic alcohol with a bluishgreen fluorescence, more readily in methylic alcohol, and very slightly in boiling water with a green fluorescence, slightly in ether with a blue fluorescence, slightly in cold but readily in hot chloroform with a reddish fluorescence, readily in acetone with a blue fluorescence, slightly in benzene with a reddish-violet fluorescence, very slightly in boiling light petroleum or carbon bisulphide, and very readily in boiling acetic acid, but without fluorescence; the solutions are all yellow except those in benzene, light petroleum, and water; the fluorescence disappears on adding acids. The *hydrochloride* is a grey, crystalline powder, and the *platinochloride, sulphate*, and *nitrate* are also described. *Paratolylpseudoazimidobenzene*, $C_6H_4Me\cdot N_3\!:\!C_6H_4$, prepared by the action of nitrous acid on the base, melts at 114°, is insoluble in water, but slightly soluble in acetic acid and in alcohol, from which it crystallises in long, white, glistening needles; it is readily soluble in acetone, and very readily in ether, chloroform, or benzene.

Metaxylylhydrazine $[Me:Me:N_2H_3 = 1:3:4]$ (Klauber, Abstr., 1891, 1362) is best prepared by reducing the diazochloride with stannous chloride, and is obtained in white, crystalline flakes, but becomes brown and oily when exposed to air and light. *Picrylmetaxylylhydrazine*, $C_6H_3Me_2\cdot NH\cdot NH\cdot C_6H_2(NO_2)_3$, prepared by the action of picryl chloride on the hydrazine, melts at 160°, crystallises from alcohol in slender, yellow needles, and dissolves in most organic solvents.

Metaxylylaznitrosodinitrobenzene, $C_6H_3Me_2 \cdot N <^{N}_{NO}> C_6H_2(NO_2)_2$, is prepared by boiling the hydrazine with acetic acid, from which it crystallises in beautiful, glistening, golden-yellow flakes; it melts at 192°, and is insoluble in water, but dissolves readily in organic solvents; its constitution is shown by the fact that it does not give the nitroso-reaction, is reduced by heating with alcohol or hydriodic acid to the pseudoazimido-compound, and is oxidised to an oxaznitroso-compound, $-N<^{-O-}_{NO}>N-$, and not to the original nitro-compound.

Metaxylylpseudoazimidodinitrobenzene, $C_6H_3Me_2 \cdot N_3 \cdot C_6H_2(NO_2)_2$, crystallises in glistening, yellow needles, melts at 125°, and is insoluble in water, but more or less soluble in organic solvents. By the action of potassium iodide and acetic acid on metaxylylaznitroso-dinitrobenzene there is produced a *compound*, $C_{14}H_{11}O_3N_5$, to which the structure $C_6H_3Me_2 \cdot N_3 \cdot C_6H_2(NO) \cdot NO_2$, or

$$NO_2 \cdot C_6H_2 <^{-N}_{-} <^{NO}_{N-} > N \cdot C_6H_3Me_2,$$ is assigned; it melts at 116°, is insoluble in water, but soluble in organic solvents, and crystallises from alcohol in slender, brown needles. *Picrylazometaxylene*,
$$C_6H_2(NO_2)_3 \cdot N_2 \cdot C_6H_3Me_2,$$
prepared by oxidising the corresponding hydrazine with chromic acid at the ordinary temperature, melts at 215—216°, crystallises in beautiful, reddish, glistening flakes, and is insoluble in water, but soluble in organic solvents.
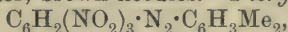
$2:4$-*Dinitrophenylmetaxylylhydrazine*, $C_6H_3Me_2 \cdot NH \cdot NH \cdot C_6H_3(NO_2)_2$, prepared by the action of *a*-chlorodinitrobenzene on $1:3:4$-meta-xylylhydrazine, crystallises from alcohol in yellow, glistening needles, decomposes at 179°, and is insoluble in water, but soluble in organic solvents. *Metaxylylaznitrosonitrobenzene*, $C_6H_3Me \cdot N <^{N}_{NO}> C_6H_3 \cdot NO_2$, crystallises from acetic acid in yellow plates and decomposes at 158°. *Metaxylylpseudoazimidonitrobenzene*, $C_6H_3Me_2 \cdot N_3 \cdot C_6H_3 \cdot NO_2$, melts at 138°, crystallises from alcohol in brownish-yellow needles, is insoluble in water, slightly soluble in ether, and readily in acetic acid, chloroform, benzene, or acetone.

$2:4$-*Dinitrophenylazometaxylene*, $C_6H_3(NO_2)_2 \cdot N_2 \cdot C_6H_3Me_2$, crystallises from acetic acid in slender, glistening, red needles, melts at 204°, is insoluble in water, slightly soluble in ether, and readily in acetic acid, chloroform, benzene, or acetone.   T. M. L.

Condensation of Aromatic Nitroso-compounds with Methylene-Derivatives. By PAUL EHRLICH and FRANZ SACHS (*Ber.*, 1899, **32**, 2341—2346).—Aromatic nitroso-compounds condense with methylene derivatives in presence of more or less alkali, to form compounds of the type $R \cdot N:CR^I R^{II}$. The compounds described in this paper are prepared by the action of nitroso-compounds on benzylic cyanide and its derivatives, and are regarded as derived from phenylazimethinephenyl,

$$<^{5\ \ 6}_{4\ \ \ \ 1}_{3\ \ 2}> -N:CH-<^{6'\ 5'}_{1'\ \ \ \ 4'}_{2'\ 3'}>.$$
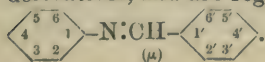
4-Dimethylamidophenyl-μ-cyanazomethinephenyl,
$$NMe_2 \cdot C_6H_4 \cdot N{:}CPh \cdot CN,$$
prepared by the action of caustic soda on a boiling alcoholic solution of
nitrosodimethylaniline and benzylic cyanide, melts at 90°, crystallises
from alcohol in long, orange-red needles with a bluish shimmer, dissolves
only slightly in most solvents in the cold, and is insoluble in water.
By the further action of alkali, a colourless *base* is produced, which
has the composition $C_{14}H_{14}ON_2$, melts at 228°, dissolves very slightly
in cold toluene, and forms a *hydrochloride* which melts at 238°. By
boiling with dilute sulphuric acid, the condensation product was
hydrolysed to benzoic cyanide (m. p. 32°) and dimethylphenylene-
diamine, which was identified by the coloration with chromic acid,
and by the methylene-blue reaction. A reduction product could not
be isolated ; zinc-dust and acetic acid gave dimethylphenylenediamine
with hydrogen cyanide and benzaldehyde, whilst zinc-dust with
calcium chloride and ammonium chloride in alcoholic solution gave
dimethylphenylenediamine, ethylic phenylacetate, and other products.

4-Diethylamidophenyl-μ-cyanazomethinephenyl,
$$NEt_2 \cdot C_6H_4 \cdot N{:}CPh \cdot CN,$$
melts at 112°, crystallises from alcohol in splendid, scarlet-golden,
glistening needles, and from ethylic acetate in large, well-formed,
garnet-like crystals, with a greenish-golden reflection, dissolves
most · readily in chloroform, fairly readily in hot alcohol, methylic
alcohol, acetone, methylal, carbon bisulphide, or ether, less readily
in light petroleum, and not at all in water. By shaking with
hydrochloric acid, the compound is decolorised, and benzoic chloride
is produced. By boiling with alcoholic potash, a *substance* is produced
which separates from alcohol in colourless crystals, melts at 172°, and
dissolves readily in acids.

4-Diethylamidophenyl-μ-cyanazomethine-4′-nitrophenyl,
$$NEt_2 \cdot C_6H_4 \cdot N{:}C(CN) \cdot C_6H_4 \cdot NO_2,$$
is produced by merely mixing nitrosodiethylaniline and paranitro-
benzylic cyanide in alcoholic solution, whilst a single drop of alkali,
ammonia, or an amine causes an extremely vigorous reaction ; it melts
at 152°, crystallises from alcohol in steel-blue, glistening needles
with a greenish reflection, which are quite opaque and only show a
violet-red colour in very thin layers ; the solutions are cherry-red, and
the vapour of the substance, which is volatile without decomposition,
is of an intense brownish-yellow colour ; it dissolves fairly readily in
chloroform, less readily in hot alcohol, acetic acid, ethylic acetate,
light petroleum, or benzene, but only slightly in these solvents in the
cold, or in ether. It dyes wool and silk directly in dilute alcoholic or
acetic acid solution, giving violet-red shades. The corresponding
compound from nitrosodimethylaniline sinters at 168° and melts at
176°, whilst that from paranitrosomethylaniline separates from
alcohol in brownish-violet, glistening crystals and melts at 186°.

<div align="right">T. M. L.</div>

**Action of Phenylhydrazine on Tricarballylic and Citric
Acids.** By C. MANUELLI and E. DE RIGHI (*Gazzetta*, 1899, **29**, ii,
148—161).—*Tricarballyldiphenylhydrazide*, obtained by the action of

two mols. of phenylhydrazine on one of tricarballylic acid, or by boiling an alcoholic solution of phenylhydrazine tricarballylate, has the constitution $N_2HPh\left\langle\begin{matrix}CO \cdot CH_2\\ CO \cdot CH \cdot CH_2 \cdot CO \cdot N_2H_2Ph\end{matrix}\right.$ It crystallises from dilute acetic acid solution in microscopic, white needles melting at 229—230°; it is almost insoluble in benzene, alcohol, chloroform, or ethylic acetate, but dissolves in hot glacial acetic acid; it is reduced by zinc dust with the formation of pyrroline. The *dibenzoyl* derivative, $C_{32}H_{26}O_5N_4$, forms an amorphous powder, which softens at 137° and melts at 140—145°. The *dinitroso*-derivative forms microscopic, yellowish-brown crystals.

Phenylhydrazine tricarballylate, $C_{18}H_{24}O_6N_4$, crystallises in minute plates melting at 180°, and is very soluble in water or alcohol, but only slightly so in benzene or ether.

Citryldiphenylhydrazide, $N_2HPh\left\langle\begin{matrix}CO \cdot CH_2\\ CO \cdot C(OH) \cdot CH_2 \cdot CO \cdot N_2H_2Ph\end{matrix}\right.$, obtained either from citric acid and phenylhydrazine or by heating phenylhydrazine citrate, separates from ethylic acetate in small, sparkling, white crystals melting at 208°; it crystallises well from orthonitrotoluene, and dissolves in glacial acetic acid with partial decomposition. The *diacetyl* derivative forms a yellowish-white, crystalline powder melting at 138°. The *dibenzoyl* derivative is obtained as an almost white, amorphous powder which melts at 129—130°, and is very soluble in all organic solvents. The *dibenzoyl-mononitroso*-derivative, $C_{32}H_{25}O_7N_5$, is a yellowish powder very soluble in organic solvents, and when purified by precipitating its benzene solution by means of light petroleum, melts and decomposes at 83—88°; with phenol and sulphuric acid, it gives Liebermann's reaction. The *nitroso*-derivative is an unstable, yellowish-red substance.

Acetylcitric acid triphenylhydrazide, $C_{26}H_{28}O_5N_6$, prepared by the action of phenylhydrazine on an ethereal solution of acetylcitric anhydride, separates from alcohol in white crystals melting at 138°. It is readily soluble in glacial acetic acid, slightly so in chloroform or alcohol, and is insoluble in ether, benzene, light petroleum, or ethylic acetate; it is decomposed on heating with dilute alkalis or mineral acids. Its *triacetyl* derivative, $C_{32}H_{34}O_8N_6$, which is deposited from alcoholic solution in small, white crystals melting at 132°, is slightly soluble in benzene, more so in alcohol or ethylic acetate, but is insoluble in light petroleum.

Phenylhydrazine citrate, $C_{18}H_{26}O_8N_4 + H_2O$, crystallises from dilute alcohol in small, white plates melting at 102°. On heating with concentrated sulphuric acid, it gives a good yield of paraphenylhydrazine-sulphonic acid. T. H. P.

Diphenylcarbamide-oxime. By ROBERT STOLLÉ (*Ber.*, 1899, **32**, 2238).—By heating with alcoholic hydroxylamine, thiocarbanilide is converted into *diphenylcarbamide-oxime*, $C_{13}H_{13}ON_3$, which melts at 151°, is soluble in acids and alkalis, and reduces ammoniacal silver oxide. A. H.

Three Crystalline Forms of Dimetanitrodiphenylcarbamide.
By A. OFFRET and HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21,
788—797).—Further study of the crystalline forms assumed by di-
metanitrodiphenylcarbamide has revealed the existence of a third
isomeric modification in addition to the two which have already been
shortly described (this vol., i, 692). The α- and β-modifications are
best obtained by slowly evaporating, in a current of dry air, a solution
in 95 per cent. alcohol of either of the three modifications, or of a
mixture thereof. In this process, the temperature [should be main-
tained nearly constant at some point between 30° and 75°, the higher
temperature being most favourable to the production of the yellow
crystals of the α-modification, whilst at lower temperatures the β-modi-
fication, which crystallises in white needles, is formed in larger pro-
portion. The third, or γ-modification, crystallises in yellow plates,
and is obtained by the spontaneous evaporation at the ordinary tem-
perature of the alcoholic mother liquors, from which the other two
modifications have been separated. The formation of the three modi-
fications depends entirely on the conditions under which crystallisation
takes place, and any one of the three forms may, by suitable regulation
of the temperature, be converted into the other two. In the presence
of alcohol, the γ-modification is stable at the ordinary temperature,
but entirely disappears at about 40°, its place being taken first by the
β-modification, which is most stable at about 50°, and then by the
α-modification, which is the most stable of the three forms. When
heated in the dry state, the α-modification remains unaltered until it
melts at 242°; the crystals of the β-modification become yellow and
opaque at 180°, and finally melt at 242°; and the yellow crystals of
the γ-modification become white and opaque at 60°, finally melting at
242°. If anhydrous acetic acid, or a mixture of alcohol and acetic
acid, is used as the solvent, the white needles of the β-modification
only are obtained on cooling the solution. This action of acids ex-
plains the fact that dimetanitrodiphenylcarbamide is obtained in the
form of a *white* powder by the action of carbonyl chloride on meta-
nitraniline, whereas when phenylic carbonate is employed a *yellow*
product is formed.

A detailed account of the crystallographic and optical properties of
the three modifications is given in the paper; each crystallises in the
monoclinic system, but the three forms are quite distinct.   N. L.

Preparation of Aromatic Thiocarbamides. By A. HUGERS-
HOFF (*Ber.*, 1899, 32, 2245—2249).—The reaction between aromatic
amines and carbon bisulphide in presence of alcohol is greatly
hastened by the presence of free sulphur. Under these conditions,
aniline, ortho- and para-toluidine, paraphenetidine, paramidophenol,
α- and β-naphthylamine, and parabromaniline can all be quantitatively
converted into the corresponding thiocarbamides in 1—2 hours. Pure
carbon bisulphide undergoes the reaction much less readily than that
which has been exposed to light, and contains free sulphur, and the
reaction also takes place more slowly when the mixture is heated in
the dark than when the preparation is carried out in the light.
Hydrogen sulphide alone does not accelerate the reaction in the same

way as free sulphur, but the exact part played by the latter has not yet been ascertained.

In some cases, a thiocarbamate is first formed when sulphur is added to the mixture of the amine with carbon bisulphide, and this then decomposes.

Paratoluidine paratolyldithiocarbamate,

$$C_6H_4Me \cdot NH \cdot CSSH, NH_2 \cdot C_6H_4Me,$$
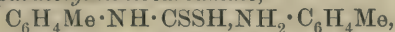
forms soft, crystalline scales, which melt and decompose at 54°. On exposure to the air, it slowly decomposes, hydrogen sulphide being evolved, sulphur liberated, and paraditolylthiocarbamide produced.

A. H.

Transformation of Alkylic Dithiocarbamates, NHR·CS·SR′, into Alkylic Imidodithiocarbonates, NR:C(SR′)₂. By EMIL FROMM and M. BLOCH (*Ber.*, 1899, **32**, 2212—2214).—It has been already shown that, whereas the groups – NH·CO·OR and – NH·CO·SR do not react in a tautomeric form, the group – NH·CS·SR in benzylic trithioimidocarboxylate does react in the tautomeric form – N:C(SH)·SR (Abstr., 1895, i, 605); it is now shown that the same group in a dithiocarbamate or urethane reacts in a similar manner. *Benzylic phenyldithiocarbamate,* NHPh·CS·S·CH₂Ph, is formed when phenylcarbimide and benzylic hydrosulphide are heated together for 7 hours at 140°; it melts at 84—85°; when treated with aqueous sodium hydroxide and benzylic chloride in equivalent proportions, it yields *dibenzylic dithiophenylimidocarbonate,* NPh:C(S·CH₂Ph)₂ ; this melts at 64—65°, and, when boiled with concentrated hydrochloric acid, yields aniline (and not benzylaniline, as the formula CH₂Ph·NPh·CS·SCH₂Ph would require) amongst the products of hydrolysis.

C. F. B.

Action of Organic Bases on Urethane. By C. MANUELLI and E. RICCA-ROSELLINI (*Gazzetta*, 1899, **29**, ii, 124—136).—Urethane reacts with metabromaniline, ortho-, meta-, and para-chloraniline, meta- and para-nitraniline, paratoluidine, nitrotoluidine [Me : NO₂ : NH₂ = 1 : 2 : 4], 1 : 3 : 4-xylidine and normal heptylamine, giving rise to the corresponding symmetrical dialkylcarbamides, thus : NH₂·COOEt + 2NH₂R = CO(NHR)₂ + NH₃ + EtOH.

With orthonitraniline, urethane does not react, the only product besides unaltered nitraniline being cyanuric acid formed by condensation of the urethane ; nitrotoluidine also [Me : NH₂ : NO₂ = 1 : 3 : 4] has no action on urethane.

Diheptylcarbamide, CO(NH·C₇H₁₅)₂, which separates from alcohol in small, white, flattened needles melting at 91°, is soluble in benzene, but insoluble in water.

T. H. P.

Action of Primary Amines on Urethanes. By C. MANUELLI and E. COMANDUCCI (*Gazzetta*, 1899, **29**, ii, 136—148).—Primary amines react with phenylurethane, giving the corresponding αβ-substituted carbamides thus : NHPh·COOEt + NH₂R = NHPh·CO·NH₂R + EtOH. Allylurethane, however, with aniline, gives symmetrical diphenylcarbamide, and with heptylamine, symmetrical diheptylcarbamide.

Phenylurethane and parachloraniline react together, forming α-phenyl-β-parachlorophenylcarbamide.

α-Phenyl-β-metabromophenylcarbamide, NHPh·CO·NH·C₆H₄Br, pre-
pared from phenylurethane and metabromaniline, crystallises from
alcohol in slender, white needles melting at 235—236°, and is almost
insoluble in ether, water, or benzene.

α-Phenyl-β-orthonitrophenylcarbamide, NHPh·CO·NH·C₆H₄·NO₂,
crystallises from water or alcohol in long needles of a pale maroon
colour melting at 231—233°.

Phenylurethane and metanitraniline give α-phenyl-β-metanitrophenyl-
carbamide.

α-Phenyl-β-paratolylcarbamide, NHPh·CO·NH·C₆H₄Me, prepared
from phenylurethane and paratoluidine, separates from alcohol in very
long, glistening, white crystals melting at 259—260°, and is soluble in
benzene or ethylic acetate, but only slightly so in ether.

α-Phenyl-β-metaxylylcarbamide, NHPh·CO·NH·C₆H₃Me₂[Me:Me:NH
=1:3:4], is deposited from alcoholic solution in minute, glistening,
white, acicular crystals melting at 242—243°; it is soluble in benzene
or acetic acid, but only very slightly so in ether or water.

α-Phenyl-βα-naphthylcarbamide, NHPh·CO·NH·C₁₀H₇, crystallises from
alcohol in slender, white, silky needles which blacken at about 274° and
melt at 277—278°; it is slightly soluble in water or chloroform, more
so in benzene.

Phenylurethane and piperidine react, forming α-phenyl-β-piperidyl-
carbamide.

α-Phenyl-β-amylcarbamide, NHPh·CO·NH·C₅H₁₁, which separates
from dilute alcohol in slender, white prisms melting at 238°, is slightly
soluble in ether, benzene, or acetic acid, and to a greater extent in
ethylic acetate.

Allylurethane, C₃H₅·NH·COOEt, obtained by the action of ethylic
chlorocarbonate on allylamine, is a colourless liquid having a density
1·004 and boiling at 194·5° under 757·27 mm. pressure.　　T. H. P.

**Resolution of Racemic Amido-acids into Optically Active
Components.** By EMIL FISCHER (*Ber.*, 1899, **32**, 2451—2471).—
Previous attempts to resolve synthetical amido-acids into optically active
components have been confined to fractional crystallisation and selective
fermentation. The compounds in question are usually so feebly acidic
and basic that their salts with alkaloids or with optically active acids do
not lend themselves to resolution by crystallisation. The author has
therefore increased the acidity of amidopropionic, aspartic, and glutamic
acids by introducing the benzoyl radicle, and then resolved the racemic
benzoyl derivatives into their optically active components by crystal-
lising certain alkaloidal salts; the active amido-acids are finally
obtained by hydrolysing the benzoyl derivatives.

l-Benzoylalanine, prepared by fractionally crystallising the brucine
salt of racemic benzoylalanine, crystallises from water in lustrous plates
and melts at 147—148° (150—151° corr.). It dissolves in 85 parts of
water at 20°, and a 1 per cent. aqueous solution has [α]_D − 3·3° at 20°.
A solution in aqueous caustic soda has [α]_D − 37·3°. The *silver*
salt is crystalline, and dissolves with difficulty in hot water; it darkens
slowly on prolonged exposure to light. *l-Alanine* crystallises from dilute
alcohol in small, colourless prisms, and melts, evolving gas, at 297°
(the racemic acid decomposes at 293°); the acid is very slightly active,

an 8·8 per cent. aqueous solution giving $a_D - 0.21°$ in a 1-decimetre tube. The *hydrochloride* crystallises in colourless needles, and has $[a]_D - 9.68°$ in aqueous solution. d-*Benzoylalanine* melts at 147—148°, and has $[a]_D + 37.13°$ in aqueous potash ; d-*alanine* forms a *hydrochloride* which has $[a]_D + 9.55°$. A cultivation of *Aspergillus niger* in an aqueous solution of racemic alanine destroys about 10 per cent. of the dextrorotatory constituent ; *Pencillium glaucum* does not flourish in a 2 per cent. solution of alanine.

Benzoyl-l-aspartic acid dissolves in 3—4 parts of hot water, and in 261 parts of water at 20°, crystallising in needles ; it melts at 180—181° (184—185° corr.), and has $[a]_D + 37.4°$ in a solution containing 2 mols. of caustic potash. *Racemic benzoylaspartic acid* crystallises from water in lustrous, colourless plates containing $1 H_2O$, and melts at 161—162° (164—165° corr.) ; the dried acid dissolves in 3—4 parts of hot water, and in 200 parts of water at 20°, but 664 parts of water at 20° are required to dissolve the crystallised acid. r-Benzoylaspartic acid may be resolved into its active components by crystallising the brucine salt. *Benzoyl*-d-*aspartic acid* melts at 180—181°, and has $[a]_D - 37.6°$ in a solution containing 2 mols. of caustic potash.

Racemic benzoylglutamic acid crystallises from hot water in colourless leaflets containing $1 H_2O$, and melts at 152—154° (155—157° corr.) ; the hydrated acid dissolves readily in alcohol, and is soluble in 124 parts of water at 20°. The *silver* salt crystallises in slender, colourless needles. When natural, optically active glutamic acid is treated with benzoic chloride in presence of aqueous sodium hydrogen carbonate, a portion of it becomes racemised. *Benzoyl-l-glutamic acid*, obtained by crystallising the strychnine salt of the racemic acid, melts at 128—130° (130—132° corr.), dissolves in less than 2 parts of boiling water, and in 21 parts of water at 20° ; a 5 per cent. aqueous solution has $[a]_D + 13.81°$, an alkaline solution, containing 2 mols. of caustic potash, having $[a]_D - 18.7°$. *Benzoyl*-d-*glutamic acid* sinters at 128°, and becomes completely fused at 137—139° ; a 10 per cent. solution containing 2 mols. of caustic potash has $[a]_D + 17.18°$. d-Glutamic acid from the benzoyl derivative has $[a]_D + 30.85°$, whilst the natural acid from casein has $[a]_D + 30.45°$.

Attempts to resolve hippuric acid into optically active components by crystallising the quinine and brucine salts were unsuccessful. Racemic benzoyltyrosine forms a brucine salt which yields an active benzoyltyrosine which melts at 163—164° (166—167° corr.), and has $[a]_D + 18.8°$ in alkaline solution. M. O. F.

Condensation Product from Isobutaldehyde and Benzaldehyde. By MILAN JOSEF STRITAR (*Monatsh.*, 1899, 20, 617—633).— An attempt was made to prepare the aldol corresponding with the glycol obtained by Swoboda and Fossek (Abstr., 1891, 31) and Reik (Abstr., 1898, i, 246) by the action of alcoholic potash on a mixture of isobutaldehyde (2 mols.) and benzaldehyde (1 mol.). It is now found that by the action of a saturated solution of potassium carbonate or of solid potassium hydroxide on this mixture a *compound*, $C_{15}H_{22}O_3$, is formed. This crystallises from glacial acetic acid in small needles melting at 94°, but its constitution is not yet determined. Reducing

agents resolve it into its constituents, but do not effect its reduction. On oxidation in pyridine solution with potassium permanganate and sulphuric acid, it yields phenylhydroxypivalic acid (Fittig and Jayne, Abstr., 1883, 471). The *phenylhydrazone*, $C_{11}H_{14}O_2N_2HPh$, is a white, crystalline powder melting at 117°, and is probably the phenylhydrazone of the required glycol.   R. H. P.

Condensation of the Cyanhydrins of Benzaldehyde and Anisaldehyde. By STEPHEN S. MINOVICI (*Ber.*, 1899, **32**, 2206—2209).— When hydrogen chloride is passed into an ethereal solution of benzaldehyde cyanhydrin, C_8H_7ON, kept at the ordinary temperature by means of cold water, a yellow *compound* is eventually precipitated which melts at 200—203° and has the composition $C_{16}H_{12}ON_2$. It has no acid properties, and forms a salt with strong hydrochloric acid; the salt, however, is decomposed at once by water. It is very stable, and attempts to decompose it into well-defined products were unsuccessful; a *monobromo-* and a *mononitro-*derivative were obtained, however; these melt at 200° and 232° respectively, and the latter is amorphous in appearance. This same product of condensation is formed when quinol or catechol is also present; in the presence of resorcinol, mandelamide results.

Anisaldehyde cyanhydrin, $C_9H_9O_2N$, under the same circumstances, reacts in a different manner, yielding a white *compound*, $C_{17}H_{15}O_3N$. The red *dibromo-*derivative of this melts and decomposes at 155°, and is converted by water or alcohol into a white substance which contains bromine and melts at 115°; the *dinitro-*derivative melts at 200°.   C. F. B.

Derivatives of Paratolualdehyde. By WENZEL HANZLIK and AL. BIANCHI (*Ber.*, 1899, **32**, 2282—2287. Compare this vol., i, 597). —*Paratoluylideneacetone*, $C_6H_4Me\cdot CH\dot{:}CH\cdot COMe$, is produced in nearly theoretical quantity by shaking paratolualdehyde, acetone, and water in a 10 per cent. solution of sodium hydroxide; it separates from light petroleum in quadratic plates, melts at 34—35°, and boils at 155—156° under 16 mm. or 277—278° under 739·4 mm. pressure, as a colourless, pleasant-smelling oil which solidifies on cooling; it is readily soluble in alcohol, ether, or carbon bisulphide, and dissolves in concentrated sulphuric acid with a blood-red coloration; the *phenylhydrazone* forms yellow leaflets melting at 138°. The *dibromide*, $C_6H_4Me\cdot CHBr\cdot CHBr\cdot COMe$, separates from light petroleum in white, crystalline crusts and melts at 84—85°.

Paratoluylideneacetophenone, $C_6H_4Me\cdot CH\dot{:}CH\cdot COPh$, prepared in the same way from paratolualdehyde and acetophenone, separates from light petroleum in pale yellow needles melting at 96·5°, and dissolves in concentrated sulphuric acid with an orange coloration which, on dilution, becomes an intense yellow; the *dibromide* forms white needles and melts at 159°; the *oxime* crystallises from alcohol in needles melting at 91°, and the *phenylhydrazone* from a mixture of ether and light petroleum in yellow needles melting at 129—130°.

Metanitroparatoluylideneacetone, $NO_2\cdot C_6H_3Me\cdot CH\dot{:}CH\cdot COMe$, prepared from metanitroparatolualdehyde and acetone, separates from alcohol in yellow needles, melts at 91°, and is readily soluble in

alcohol, ether, carbon bisulphide, or chloroform; it is coloured red by concentrated sulphuric acid and forms an orange coloured solution showing a green fluorescence. The *dibromide* forms flat crystals melting at 112—113°, and the *phenylhydrazone* crystallises from alcohol in well-formed, red crystals melting at 146—147°.

Metanitroparatoluylideneacetophenone, $NO_2 \cdot C_6H_3Me \cdot CH\!:\!CH \cdot COPh$, prepared from metanitroparatolualdehyde and acetophenone, separates from alcohol in yellow leaflets, melts at 142—143°, and is coloured red by concentrated sulphuric acid, forming an orange-coloured solution; the *dibromide* crystallises from carbon bisulphide and melts at 171—172°, the *oxime* from alcohol in small, well-formed crystals melting at 71—72°, and the *phenylhydrazone* from alcohol in brick-red leaflets melting at 119°.

On treatment with sodium acetate and acetic anhydride at 150°, metanitroparatolualdehyde yields *metanitroparamethylcinnamic acid*, $NO_2 \cdot C_6H_3Me \cdot CH\!:\!CH \cdot COOH$, which separates from dilute alcohol in long, slender needles and melts at 170—171°; it is readily soluble in alcohol, hot water, or ether, and forms a white, insoluble *silver* salt; the *methylic* and *ethylic* salts crystallise from a mixture of ether and light petroleum, the former in long, white needles melting at 108—109°, and the latter in monoclinic leaflets melting at 96—97°.

The formation of metanitroparamethylcinnamic acid in this reaction is preceded by the production of *metanitroparatoluylidene diacetate*, $NO_2 \cdot C_6H_3Me \cdot CH(OAc)_2$, since this substance separates on the addition of an equal weight of acetic anhydride to the nitro-aldehyde; it crystallises from a mixture of ether and light petroleum in monoclinic plates, melts at 98—98·5°, and on treatment with anhydrous sodium acetate and acetic anhydride yields the corresponding cinnamic acid. On treating paramethylcinnamic acid with a mixture of concentrated sulphuric acid and nitric acid, it is transformed into 4-*methyl-3-dinitro-styrene*, $NO_2 \cdot C_6H_3Me \cdot CH\!:\!CH \cdot NO_2$, which forms short, yellow needles melting at 117—118°, and on oxidation with potassium permanganate yields nitroterephthalic acid, or with dilute nitric acid, metanitroparatoluic acid.

J. F. T.

Preparation of Aromatic Aldehydes and the Artificial Preparation of Indigo Dyes. By MICHAËL I. KONOWALOFF (*Chem. Centr.*, 1899, i, 1074—1075; from *J. Russ. Chem. Soc.*, 1899, **31**, 54—56).—Mesitylaldehyde melts at 9° and boils at 220—222°. The aldehydes, prepared by the method previously described (*J. Russ. Chem. Soc.*, 1898, **30**, 960), were nitrated. The nitro-group enters into the benzene ring in the ortho-position when the meta-position is occupied by organic radicles. All the orthonitro-compounds so prepared, when treated with acetone and alkali, yielded homologues of indigo. Dimethyl-, tetramethyl-, and dimethylditertiarybutyl-indigo were prepared.

E. W. W.

Experiments on the Synthesis of Chrysin Derivatives. By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1899, **32**, 2260—2269).—In the hope of effecting a synthesis of chrysin, the method of Emilewicz and von Kostanecki (Abstr., 1898, i, 369) for the synthesis of oxyflavones was applied to the phloroglucinol series;

it was found, however, that only coumaranone derivatives could be obtained from the condensation product of phloracetophenone dimethylic ether with benzaldehyde.

Phloracetophenone trimethylic ether, $C_6H_2(OMe)_3 \cdot COMe$, obtained by the action of acetic chloride on phloroglucinol trimethylic ether in the presence of sublimed ferric chloride, forms broad prisms, which, when recrystallised from dilute alcohol, melt at 100°; on treatment with aluminium chloride at 110°, it is converted into *phloracetophenone dimethylic ether,* $OH \cdot C_6H_2(OMe)_2 \cdot COMe$ [$OH : (OMe)_2 = 2 : 4 : 6$], which separates from dilute alcohol in leaflets melting at 82—83°. The *acetyl* compound crystallises from alcohol in prisms and melts at 107°.

Phloracetophenone triethylic ether, $C_6H_2(OEt)_3 \cdot COMe$, prepared in the same way as the trimethylic ether, forms rhombic plates and melts at 75°; with aluminium chloride, it yields the corresponding *diethylic ether,* which separates from dilute alcohol in needles melting at 85°.

[With T. EMILEWICZ.]—2'-*Hydroxy*-4': 6'-*dimethoxychalkone,*
$$OH \cdot C_6H_2(OMe)_2 \cdot CO \cdot CH\text{:}CHPh,$$
prepared by the action of phloracetophenone dimethylic ether on benzaldehyde in alcoholic sodium hydroxide solution, separates from alcohol in yellow, concentric needles melting at 91—92°, which are coloured orange by concentrated sulphuric acid, and give a yellow to light orange solution. The *sodium* derivative is deep yellow, and is dissociated by water. The *acetyl* derivative separates in leaflets melting at 129—130°, and on bromination passes into 2'-*acetoxy*-4': 6'-*dimethoxybromochalkone dibromide,* $OAc \cdot C_6HBr(OMe)_2 \cdot CO \cdot CHBr \cdot CHPhBr$, which crystallises in leaflets, and when rapidly heated melts at 185°, decomposing above this temperature with evolution of gas.

1 : 3-*Dimethoxybenzylidenebromocoumaranone,*

$$C_6HBr(OMe)_2 \diagdown_{CO}^{O} \diagup C\text{:}CH \cdot Ph,$$
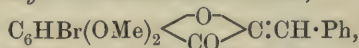
from the dibromide and alcoholic potassium hydroxide, separates from benzene in white needles melting at 223°, and dissolves in concentrated sulphuric acid with an orange coloration.

[With B. BEDNARSKI.]—2'-*Hydroxy*-4': 6'-*diethoxychalkone,*
$$OH \cdot C_6H_2(OEt)_2 \cdot CO \cdot CH\text{:}CH \cdot Ph,$$
prepared from phloracetophenone diethylic ether and benzaldehyde, separates from alcohol in deep yellow, concentrically grouped needles, and melts at 118—119°; concentrated sulphuric acid colours the crystals orange, and forms a yellow solution; the *acetyl* compound crystallises from dilute alcohol in yellow plates melting at 25°, and on bromination in carbon bisulphide solution gives 2'-*acetoxy*-4': 6'-*diethoxybromochalkone dibromide,* $OAc \cdot C_6HBr(OEt)_2 \cdot CO \cdot CHBr \cdot CHPhBr$, which forms leaflets melting and decomposing at 169—170°, and on treatment with alcoholic potassium hydroxide yields 1 : 3-*diethoxybenzylidenebromocoumaranone,* $C_6HBr(OEt)_2 \diagdown_{CO}^{O} \diagup C\text{:}CHPh$, which separates from benzene in short, yellow needles melting at 205°, and behaves towards sulphuric acid similarly to the dimethoxy-derivatives.

[With F. HERSTEIN.]—With the view of synthesising luteolin,

which according to A. G. Perkin is 1 : 3 : 3′ : 4′-tetrahydroxyflavone, phloracetophenone dimethylic ether was condensed with piperonal, but as in the previous instance coumaranone derivatives alone were formed.

2′-*Hydroxy* 4′ : 6′-*dimethoxy*-3 : 4-*methylenedioxychalkone*,

$$\text{OH·C}_6\text{H}_2(\text{OMe})_2\text{·CO·CH:CH·C}_6\text{H}_3\underset{O}{\overset{O}{<}}\text{CH}_2,$$
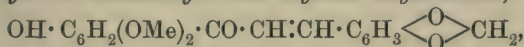
the first product of the condensation, separates from alcohol in clusters of slender needles and melts at 162—163°; with concentrated sulphuric acid, the crystals become coloured a fine red, the solution, however, quickly becoming opaque. The *acetyl* derivative separates from dilute alcohol in leaflets melting at 120—121°, and on bromination in chloroform solution gives 2′-*acetoxy*-4′ : 6′-*dimethoxy*-3 : 4-*methylenedioxydibromochalkone*,

$$\text{OAc·C}_6\text{HBr}(\text{OMe})_2\text{·CO·CBr:CH·C}_6\text{H}_3\underset{O}{\overset{O}{<}}\text{CH}_2,$$
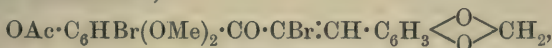
which separates from a mixture of chloroform and alcohol in plates melting and decomposing at 168°. The constitution of this compound follows from the fact that, on treatment with alcoholic potash, it is converted into 1 : 3-*dimethoxypiperonalbromocoumaranone*,

$$\text{C}_6\text{HBr}(\text{OMe})_2\underset{CO}{\overset{O}{<}}\text{C:CH·C}_6\text{H}_3\underset{O}{\overset{O}{<}}\text{CH}_2,$$
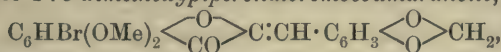
which separates from glacial acetic acid or a mixture of pyridine and alcohol as a crystalline precipitate, and melts at 274°, the solution in the latter solvent showing a marked green fluorescence. In concentrated sulphuric acid, it dissolves to a carmine red solution. J. F. T.

Aromatic Nitro-compounds : Substitution of Nitro-groups by Methoxyl and Ethoxyl. By W. REINDERS and W. E. RINGER (*Rec. Trav. Chim.*, 1899, **18**, 326—329).—*Paramethoxybenzonitrile*, prepared by boiling a solution of paranitrobenzonitrile and sodium methoxide in methylic alcohol, and purified by distillation in steam and crystallisation from alcohol, separates in white needles, melts at 59°, and boils at 137·6° under 18·5 mm. pressure, and at 240·1° under ordinary pressure ; its boiling points under intermediate pressures are also given. The substance is very soluble in the ordinary organic solvents, and is hydrolysed by caustic soda to paramethoxybenzoic acid.

Parethoxybenzonitrile, obtained by heating paranitrobenzonitrile with a dilute alcoholic solution of sodium ethoxide, crystallises in white needles and melts at 57°.

In the case of the methoxy-derivative, the yield is practically quantitative, but with the ethoxy-compound it is only 10 per cent. of that theoretically possible.　　　　　　　　　　　　　　G. T. M.

Orthomethoxybenzonitrile and Orthethoxybenzonitrile. By W. E. RINGER (*Rec. Trav. Chim.*, 1899, **18**, 330—333).—*Orthomethoxybenzonitrile*, produced by heating a methylic alcoholic solution of orthonitrobenzonitrile with excess of sodium methoxide, is obtained as an oil, which, when cooled in a mixture of alcohol and solid carbonic anhydride, solidifies to a mass of crystals melting at 24·5°; it boils at 140° under 18 mm. pressure, and at 260° under ordinary pressure;

its boiling points under intermediate pressures are also recorded. The substance is not hydrolysed by boiling with 25 per cent. hydrochloric acid or 50 per cent. caustic potash, but when boiled with 50 per cent. sulphuric acid, it is converted into salicylic acid.

Orthethoxybenzonitrile melts at 5° and boils at 153·5° under 29 mm. and at 263·5° under 766 mm. pressure; other intermediate boiling points are also recorded. It is not attacked when boiled with 50 per cent. sulphuric acid, but a trace of salicylic acid is produced on boiling with acid of 70 per cent.   G. T. M.

Action of Iodine on Cinnamic Acid in Pyridine Solution. By GIOVANNI ORTOLEVA (*Gazzetta*, 1899, **29**, i, 503—509).—*Pyridine β-iodocinnamate*, $C_{14}H_{12}O_2NI$, obtained by the interaction in molecular proportion of a pyridine solution of cinnamic acid and an alcoholic solution of iodine, melts and decomposes at 165—166°, is insoluble in alcohol, ether, or benzene, slightly soluble in boiling water, and dissolves slowly in alkalis with elimination of pyridine. It is soluble in dilute mineral acids, especially on heating, and separates unchanged in glistening, white scales. Treated with sodium hydroxide solution, it yields benzoylacetic acid and acetophenone.

β-Iodocinnamic acid, $CPhI\!:\!CH\cdot COOH$, obtained by decomposing a sodium hydroxide solution of the pyridine salt with sulphurous acid, crystallises from benzene in white needles which melt at 160—162° and in the air assume a yellowish coloration; it is only slightly soluble in water, but dissolves in alcohol or ether, and in sodium carbonate solution with effervescence. It decolorises potassium permanganate in the cold, and gives no coloration with ferric chloride. The *calcium* salt, $(C_9H_6O_2I)_2Ca + 3\tfrac{1}{2}H_2O$, crystallises in short, colourless needles, and the *silver* salt, in glistening, white scales, which on heating decompose with the formation of phenylacetylene, silver iodide, and carbonic anhydride.   T. H. P.

Monobromotruxone from α-Bromallocinnamic Acid. By W. MANTHEY (*Ber.*, 1899, **32**, 2475—2476. Compare Abstr., 1882, 615, and 1898, i, 662).—Leuckart gave to the substance obtained by treating α-bromallocinnamic acid with cold concentrated sulphuric acid the composition $C_{17}H_{12}O_2Br_2$; in reality, it is a monobromotruxone, for on heating for 3 hours at 180° with hydriodic acid and red phosphorus, it is reduced to truxene, the latter being identified by oxidation to tribenzoylenebenzene (Abstr., 1878, 229; 1890, 514; 1898, i, 32).

On reducing monobromotruxone with zinc dust and acetic acid, Leuckart obtained a compound to which he ascribed the composition $C_{17}H_{14}O_2$; his analytical results, however, approximate to those required for the formula for a dihydrotruxone, C_9H_8O.   G. T. M.

Preparation of Dibromindone from α-Dibromocinnamic Acid. By THEODOR LANSER (*Ber.*, 1899, **32**, 2477—2478).—By adding bromine to phenylpropiolic acid, αβ-dibromocinnamic and αβ-dibromoallocinnamic acids are produced; on treatment with concentrated sulphuric acid, the latter yields dibromindone, whilst the former remains unaltered; the current hypothesis of the stereochemical

relationship of these compounds furnishes a ready explanation of this result (compare Abstr., 1898, i, 662). In accordance with this view, it should be possible, either by distillation or other energetic treatment, to convert the dibromocinnamic acid, $\begin{smallmatrix} Ph\cdot C\cdot Br \\ || \\ Br\cdot C\cdot COOH \end{smallmatrix}$ (α-acid, m.p. 139°), into the dibromallocinnamic acid, $\begin{smallmatrix} Ph\cdot C\cdot Br \\ || \\ COOH\cdot C\cdot Br \end{smallmatrix}$ (β-acid, m.p. 100°), just as fumaric and allocinnamic acids are converted into their stereoisomerides. The α-acid, which is not acted on by sulphuric acid, gives an 80 per cent. yield of dibromindone when distilled with phosphoric anhydride under 20 mm. pressure. Phenylpropiolic acid hydrobromide, when similarly treated, yields monobromindone; this compound crystallises from dilute acetic acid in canary-yellow needles melting at 64—65°, is extremely soluble in all organic solvents, and decomposes spontaneously when left in the desiccator.   G. T. M.

Optical Resolution and Properties of Mandelic Acid. By EBERHARD RIMBACH (*Ber.*, 1899, **32**, 2385—2391. Compare Lewkowitsch, Abstr., 1883, **44**, 1124).—A solution of mandelic acid and crystallised cinchonine in water is heated on the water-bath for an hour with constant shaking; the whole is allowed to remain overnight, and then separated from resinous matter by filtration; on adding crystals of cinchonine *d*-mandelate to the clear solution, kept at a temperature of 6—8°, a separation of the dextromandelate occurs. If strong brine is added to the mother liquor, a copious precipitate of conchonine hydrochloride is produced, but this subsequently induces the gradual separation of a considerable quantity of cinchonine *d*-mandelate.

Dextromandelic acid melts at 133·8° and crystallises in hemimorphic, monoclinic crystals $[a:b:c = 1\cdot4180:1:2\cdot9269\; ;\; \beta = 102° 54' 43'']$; its specific rotatory power at 20° is $[\alpha]_D + 215\cdot51 - 0\cdot5777q$. The rotational dispersion is normal, but rather strong, the dispersion coefficient, $[\alpha]_D$ blue/$[\alpha]_D$ red, being, as a mean, 2·72. (Cane sugar, for an equal wave-length interval, has a coefficient of 2·33, and santonin of 2·96.) A mixture of dextromandelic acid with ordinary inactive mandelic acid in certain proportions has a melting point lower than that of either of its constituents; moreover, the solubility of inactive mandelic acid is increased by the addition of dextro-acid, and the solution becomes optically active. Inactive mandelic acid is therefore a racemic compound at the ordinary temperature, and no indication of a transition point has as yet been obtained.

Cinchonine lævomandelate, obtained from the mother liquor from the dextromandelate, had $[\alpha]_D + 92\cdot1$ at 20° in Hesse's liquid (1 volume of alcohol and 2 volumes of chloroform). It forms large, hemihedral, orthorhombic crystals $[a:b:c = 0\cdot7123:1:1\cdot8252]$. Cinchonine dextromandelate has $[\alpha]_D + 152\cdot4$ at 20°, and could not be obtained in measurable crystals. The solubilities of both salts have been determined at several temperatures; at higher temperatures, the solubility curves approach one another, hence the necessity for the precaution of maintaining a low temperature in effecting the separation of the two compounds; lower temperatures than those above

recommended lead to impure separations, due, perhaps, to the formation of a partially racemic compound. A. L.

Stereoisomeric Phenylbromolactic Acids. By EMIL ERLENMEYER, jun., and A. MOEBES (*Ber.*, 1899, **32**, 2375—2377).—The authors give details of the resolution of α-bromophenyllactic acid into its optically active components by means of cinchonine (compare Abstr., 1891, 1482). The *salt*, $C_{28}H_{31}O_4N_2Br$, of the dextro-acid is less soluble in alcohol than that of the lævo-acid, and forms slender, white needles which decompose at 159—160°; the *dextro*-acid crystallises from chloroform in measurable crystals, melts at 119—120°, and has $[\alpha]_D + 21\cdot46$ in absolute alcohol. The *lævo*-acid could not be obtained pure; as isolated, it melted at 118—119°, and had $[\alpha]_D - 15\cdot55$, showing that it was contaminated with the dextro-modification. Taking into account the preparation of α-bromophenyllactic acid from cinnamic acid, $\begin{array}{c} H\cdot C\cdot Ph \\ H\cdot C\cdot COOH \end{array}$, the authors assign to its optically active components the configurations

$$\begin{array}{ccc} C_6H_5 & & C_6H_5 \\ H\cdot C\cdot OH & & HO\cdot C\cdot H \\ H\cdot C\cdot Br & \text{and} & Br\cdot C\cdot H \\ COOH & & COOH. \end{array}$$
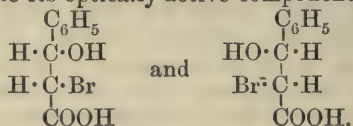
W. A. D.

Synthesis of Parisopropylphenylhydroxypivalic Acid. By L. SSAPOSCHNIKOFF (*Chem. Centr.*, 1899, i, 1204; from *J. Russ. Chem. Soc.*, 1899, **31**, 250—254).—A 75 per cent. yield of crude *parisopropylphenylpivalic acid*, $C_6H_4Pr\cdot CH(OH)\cdot CMe_2\cdot COOH$, is obtained by the action of the zinc–copper couple on ethylic bromisobutyrate and cuminol at 50°. The acid crystallises from water or aqueous alcohol in transparent needles, is only very slightly volatile in steam, melts at 106°, is very slightly soluble in cold water, and easily so in alcohol, ether, benzene, or glacial acetic acid. A determination of the molecular weight gave 224. The *sodium* salt crystallises with $3H_2O$, the *barium* and *calcium* salts with $4H_2O$, whilst the *potassium* and *silver* salts are anhydrous. All these salts are soluble in hot water, but sparingly so, or insoluble in cold water. The *copper*, *mercury*, and *lead* salts are insoluble in cold water. By distilling the acid with a 25 per cent. solution of sulphuric acid, parisopropylisobutenylbenzene, boiling at 236—238° (compare Perkin, Trans., 1879, **35**, 141), is formed.

E. W. W.

Ethylic Benzalanilacetoacetate [Anilinobenzylacetoacetate]. By CORRADO BERTINI (*Gazzetta*, 1899, **29**, ii, 22—35).—*Dibenzalacetoneaniline* [*anilidobenzylbenzylideneacetone*], $CHPh\colon CH\cdot CO\cdot CH_2\cdot CHPh\cdot NHPh$, prepared by the interaction of dibenzylideneacetone and aniline in molecular proportion, separates from benzene in well-developed, lustrous yellow crystals melting at 129—130°. When warmed with dilute hydrochloric acid, it decomposes, with formation of benzaldehyde.

Ethylic anilidobenzylacetoacetate oxime,

$$NOH\colon CMe\cdot CH(CHPh\cdot NHPh)\cdot COOEt,$$
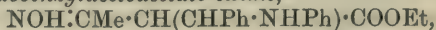
prepared by the action of a sodium hydroxide solution of benzaldehyde

on a mixture of hydroxylamine hydrochloride, aniline, and ethylic acetoacetate, exists in two modifications. If the crude product of the reaction is rapidly heated with dilute alcohol so as to leave some undissolved, and the solution cooled, a white substance is obtained which melts at 136—137°, and is soluble in the ordinary solvents and in hot dilute hydrochloric acid, but insoluble in alkalis, and only slightly soluble in water. This form, which, if not very pure, reddens in the air, does not yield an acetyl derivative. If, however, the original product of the reaction is treated with cold alcohol, on filtering off the latter a white substance remains, which, when crystallised from boiling benzene, or precipitated from its solution in acetone by adding alcohol, forms a colourless, crystalline powder melting and decomposing at 153°; it is insoluble in dilute sodium hydroxide solution or dilute hydrochloric acid, slightly soluble in benzene or light petroleum, and less soluble in alcohol than the other isomeride into which it is gradually converted on keeping. The oxime, melting at 153°, forms an *acetyl* derivative, $C_{19}H_{21}O_2N\!:\!NOAc$, which crystallises from dilute alcohol in long, shining needles melting at 114°.

The *phenylhydrazone* also exists in two forms, probably the *syn-* and *anti-*modifications. One of them is a sandy, white, non-crystalline powder which, when purified by dissolving in chloroform and precipitating with light petroleum, melts and decomposes at 79—80°. It is insoluble in water, ether, or sodium hydroxide solution, but dissolves slightly in benzene or light petroleum, and more so in alcohol or chloroform; on heating with dilute hydrochloric acid, decomposition takes place with the separation of benzaldehyde. From the benzene-light petroleum mother liquors of this oxime, another form is slowly deposited which separates from alcohol in shining, white crystals melting at 138—139° with decomposition.

On heating ethylic anilidobenzylacetoacetate with a mixture of equal volumes of glacial acetic acid and alcohol, a *substance* is obtained which has the composition $C_{16}H_{15}ON$, and separates from benzene in large, well-developed crystals melting at 155—156°; in benzene solution, it gives a molecular weight corresponding with the formula $C_{32}H_{30}O_2N_2$. It is a very stable, neutral compound, and is unchanged by boiling with alcoholic hydroxylamine or its hydrochloride; it dissolves in boiling acetic anhydride, but does not separate unaltered. When dissolved in carbon bisulphide, it takes up bromine with evolution of heat, and with iodine it forms a compound containing 42·6 per cent. of iodine.

A quantity of moist ethylic anilidobenzylacetoacetate, when kept in a closed vessel for about six months, changed spontaneously into the diethylic diphenyldihydrodicarbolutidinate obtained by Lachowicz by the prolonged action, at the ordinary temperature, of 2 mols. of aniline and 2 mols. of benzaldehyde on an alcoholic solution of 1 mol. of ethylic acetoacetate.

On the dry distillation of ethylic anilidobenzylacetoacetate, a considerable quantity of symmetrical diphenylcarbamide is formed.

T. H. P.

Alkylmalononitriles and their Derivatives. By JOHN C. HESSLER (*Amer. Chem. J.*, 1899, **22**, 169—198).—The product obtained

by the interaction of ethylic cyanacetate, sodium ethoxide, and ethylic iodide in alcoholic solution (Henry, *Jahresber.*, 1889, 637) contains 70 per cent. of ethylic ethylcyanacetate and 30 per cent. of ethylic diethylcyanacetate; the amount of the latter is diminished by carrying out the action in ethereal solution. On leaving the crude mixture in contact with aqueous ammonia during 24 hours, ethylcyanacetamide (Henry, *loc. cit.*) is formed, whilst the *ethylic diethylcyanacetate* is not acted on and can be isolated by distilling under diminished pressure; it is a colourless liquid which boils at 110—112° under 24 mm., and at 215—216° under ordinary pressure, and when heated with concentrated hydrochloric acid at 100° yields diethylcyan-acetic acid (Hesse, Abstr., 1897, i, 16). *Ethylcyanacetic acid*, $CN \cdot CHEt \cdot COOH$, prepared by treating crude ethylic ethylcyanacetate in ethereal solution with aqueous caustic soda, which, under these conditions, does not act on the diethylcyanacetate present, is a hygroscopic liquid; it boils at 160—161° under 24 mm., but when distilled under the ordinary pressure is decomposed into carbonic anhydride and butyronitrile; the *silver* salt, $C_5H_6O_2NAg$, is a white, crystalline powder which blackens on keeping. Pure ethylic ethylcyanacetate, $CN \cdot CHEt \cdot COOEt$, prepared by warming the silver salt with ethylic iodide, boils at 207—209° and has a sp. gr. 0·985 at 22·3°.

When ethylic cyanacetate is treated with benzylic chloride (1 mol.) and sodium according to the Conrad-Limpach method, ethylic dibenzylcyanacetate (compare Cassirer, Abstr., 1893, i, 16) is formed together with about 20 per cent. of *ethylic benzylcyanacetate*, $CN \cdot CH(CH_2Ph) \cdot COOEt$; the latter, however, is the principal product of the action of benzylic chloride on dry ethylic sodiocyanacetate at 80°. It is a colourless oil which boils at 176—183° under 20 mm. pressure, and is not acted on by aqueous sodium carbonate; with cold caustic soda, it yields sodium benzylcyanacetate, but, on warming, sodium benzylmalonate is formed. Ethylic dibenzylcyanacetate is a viscid, yellow syrup which boils at 237° under 25 mm. pressure, and solidifies after several weeks to large, colourless crystals melting at 33° (compare Cassirer, *loc. cit.*).

Benzylcyanacetamide, $CN \cdot CH(CH_2Ph) \cdot CO \cdot NH_2$, prepared by the action of ammonia on ethylic benzylcyanacetate, crystallises from alcohol in large, colourless prisms and melts at 130°; it is stable in presence of aqueous sodium carbonate, but is rapidly hydrolysed by caustic soda. When distilled with phosphorus pentachloride under 20 mm. pressure, it yields *benzylmalononitrile*, $CH_2Ph \cdot CH(CN)_2$, which crystallises from alcohol in large, white rhombohedra, from water or light petroleum in needles, melts at 91°, and boils at 174° under 23 mm. pressure; when treated with sodium in benzene solution, it yields the *sodium* derivative, $CH_2Ph \cdot C(CN):C:NNa$, in the form of a white, amorphous powder, which is decomposed by water, regenerating benzylmalonitrile, and when heated at 120° under 20 mm. pressure yields hydrocinnamonitrile together with sodium cyanide and the so-called azulmic acid. *Silver benzylmalononitrile*, $CH_2Ph \cdot C(CN):C:NAg$, prepared by adding dilute caustic potash drop by drop to a mixture of benzylmalononitrile and silver nitrate dissolved in 66 per cent. alcohol,

is a white, amorphous powder which is stable in dry, but is rapidly decomposed by moist air; when heated at 80°, it yields silver cyanide and a resinous substance, and is converted by aqueous potassium cyanide into benzylmalononitrile, probably through the stages.

I. $CH_2Ph \cdot C(CN) \vdots C \vdots NAg + H_2O \longrightarrow CH_2Ph \cdot CH(CN) \cdot C(OH) \vdots NAg$
$\longrightarrow CH_2Ph \cdot CH(CN) \cdot CN + AgOH.$

II. $AgOH + KCN = AgCN + KOH.$
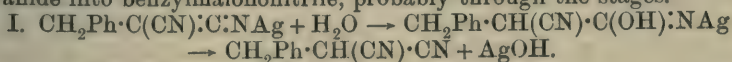
Ethylmalononitrile (compare Henry, *loc. cit.*), $CHEt(CN)_2$, prepared from ethylcyanacetamide and phosphorus pentachloride, is a colourless oil which boils at 90—91° under 20 mm. and at 200° under ordinary pressure, and darkens on keeping; it dissolves in cold caustic soda, yielding sodium ethylcyanacetate, which, on heating, is converted into sodium ethylmalonate. It is only slowly acted on by sodium in ethereal or benzene solution; neither the sodium nor the silver derivative could be isolated.

Dibenzylmalononitrile,* $C(CH_2Ph)_2(CN)_2$, prepared by the action of alcoholic sodium ethoxide and benzylic chloride on malononitrile dissolved in absolute alcohol, is a white, crystalline solid which melts at 131° and is not acted on by aqueous alkalis. A poor yield of a mixture of mono- and di-benzylmalononitriles is obtained on heating dry sodium malononitrile with benzylic chloride.

Benzylcyanacetic acid (*α-cyano-β-phenylpropionic acid*),
$$CH_2Ph \cdot CH(CN) \cdot COOH,$$
prepared by hydrolysing its ethylic salt, is a white, crystalline solid which melts at 101—102° and, when distilled, decomposes into carbonic anhydride and hydrocinnamonitrile; the *silver* salt is a heavy, white solid which darkens slowly in the light and melts and decomposes at 140°.
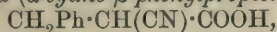
Benzoylbenzylmalononitrile, $CH_2Ph \cdot CBz(CN)_2$, separates as a crystalline mass on mixing benzoic chloride with sodium benzylmalononitrile in cold absolute ether; it is sparingly soluble in light petroleum, melts at 100°, and is not acted on by water or aqueous sodium carbonate, but is decomposed by alcohol or aqueous sodium hydroxide, the benzoyl group being removed.

Bromobenzylmalononitrile, $CH_2Ph \cdot CBr(CN)_2$, prepared by adding sodium benzylmalononitrile to bromine dissolved in ether, crystallises from alcohol in thin plates with serrated edges, from light petroleum in needles, and melts at 119—120°; it is not acted on by aqueous caustic soda, but when heated alone decomposes, the distillate apparently consisting of benzylidenemalononitrile.

Ethylic benzyldicyanacetate, $CH_2Ph \cdot C(CN)_2 \cdot COOEt$, formed by the interaction of sodium benzylmalononitrile and ethylic chloroformate in cold absolute ether, crystallises from a mixture of ether and light petroleum in large, colourless prisms, and melts at 44—45°.

Methylbenzylmalononitrile, $CH_2Ph \cdot CMe(CN)_2$, obtained by the action of methylic iodide on the silver or sodium derivative of benzylmalononitrile, crystallises from water in needles and from light petroleum in large prisms, and melts at 94—95°. When, however, methylic iodide is added to an alcoholic solution of benzyl-

* Dibenzylmalononitrile has been prepared by Errera and Berté (Abstr., 1897, i, 18), but no reference is made to this fact in the paper.—W. A. D.

malononitrile and sodium ethoxide, *benzylmethylcyanacetimidoethyl ether*, $CH_2Ph \cdot CMe(CN) \cdot C(OEt)\dot:NH$, is formed instead of the expected nitrile; it boils at 170° under 22 mm., at 156° under 9 mm. pressure, and can also be obtained by the action of alcoholic sodium ethoxide on benzylmethylmalononitrile. *Benzylethylcyanacetimidoethyl ether*, $CH_2Ph \cdot CEt(CN) \cdot C(OEt)\dot:NH$, prepared from either ethyl- or benzyl-malononitrile, boils at 170° under 22 mm. pressure.

Phenylacetimidoethyl ether, $Ch_2Ph \cdot C(OEt)\dot:NH$, prepared from the hydrochloride by Bushong's method (Abstr., 1896, i, 546), boils at 105—106° under 10 mm. pressure (compare Lückenbach, Abstr., 1884, 1134); *ethylic monimidomalonate*, $COOEt \cdot CH_2 \cdot C(OEt)\dot:NH$, prepared by adding the hydrochloride obtained by Pinner's method (Abstr., 1895, i, 264) to 10 per cent. aqueous caustic potash, distils without change under diminished pressure, but decomposes when heated at 165°.   W. A. D.

Synthesis of Unsaturated Dicarboxylic Acids from Ketones and Diethylic Succinate. By HANS STOBBE (*Annalen*, 1899, **308**, 67—88. Compare Abstr., 1896, i, 234, and 1897, i, 192).—In a former paper (Abstr., 1895, i, 142), the author has shown that when acetophenone and methyl ethyl ketone undergo condensation with diethylic succinate, two isomeric acids are produced in each case. Those melting at the higher temperature decompose on fusion, and were regarded as substituted itaconic acids, for example, γ-methyl-phenylitaconic acid, $CMePh\dot:C(COOH) \cdot CH_2 \cdot COOH$, from acetophenone; the isomeric acids, melting without decomposition, were called aticonic acids, and were looked upon as being stereoisomeric. Subsequent investigation, however, has rendered it more probable that they are structurally isomeric, having the unsaturated linking in the γδ-position relative to the first carboxylic group; this refers them to pyrotartaric acid, and the substance formerly called phenylmethylaticonic acid becomes *γ-phenyl-γ-methylenepyrotartaric acid*, $CH_2\dot:CPh \cdot C(COOH) \cdot CH_2 \cdot COOH$. The class name γ-alkylenepyrotartaric acid is chosen to represent those acids which do not decompose on fusion (compare Fittig, this vol., i, 332).

The following abstracts contain descriptions of the acids obtained by condensing other ketones with diethylic succinate. According to the constitution of the ketone, condensation gives rise either to a single itaconic acid, a single alkylenepyrotartaric acid, or a mixture of both acids. Thus, benzophenone yields γ-diphenylitaconic acid as sole product, whilst acetophenone gives rise to γ-phenyl-γ-methylita-conic, γ-phenyl-γ-methylisoitaconic, and γ-phenyl-γ-methylenepyro-tartaric acids; deoxybenzoin and dibenzyl ketone yield γ-phenyl-γ-benzylidenepyrotartaric acid and γ-benzyl-γ-benzylidenepyrotartaric acid respectively.

Theoretical considerations occupy the remaining portion of the paper.   M. O. F.

Condensation of Benzophenone with Diethylic Succinate. By HANS STOBBE (*Annalen*, 1899, **308**, 89—114. Compare Abstr., 1896, i, 234).—Ethylic hydrogen diphenylitaconate, obtained by con-densing benzophenone with diethylic succinate under the influence of

sodium ethoxide, has been already described (*loc. cit.*); the *sodium* and *calcium* salts are anhydrous. *Ethylic β-bromo-γ-diphenylparaconate*, formed when the foregoing ethereal salt is treated with bromine water, crystallises from light petroleum in lustrous prisms, and melts at $95 \cdot 5$—$96 \cdot 5°$. Diphenylitaconic acid crystallises from benzene in needles containing $\frac{1}{2}$ mol. of the solvent, whilst ether deposits it in lustrous, monoclinic crystals, containing 1 mol. of the solvent ; the *sodium* salt contains $2H_2O$, and the *calcium*, *barium*, and *silver* salts are anhydrous.

[With PAUL KOHLMANN.]—The *anhydride* of γ-diphenylitaconic acid crystallises from petroleum in large, colourless prisms, and melts at 151—$152°$.

γ-Diphenylpyrotartaric acid, $CHPh_2 \cdot CH(COOH) \cdot CH_2 \cdot COOH$, prepared by reducing diphenylitaconic acid with sodium amalgam, separates from water in fibrous crystals containing $1H_2O$; in this condition, it melts indefinitely between $145°$ and $180°$, but the anhydrous acid melts at 180—$184°$. The *calcium* salt contains $2H_2O$, and the barium salt $1H_2O$, whilst the silver salt is anhydrous.

When diphenylitaconic acid is oxidised in alkaline solution with potassium permanganate, benzophenone is regenerated ; the other products are oxalic and benzoic acids.

[With MAX NOETZEL.]—*γ-Diphenylaconic (γ-diphenylcrotonolactone-carboxylic) acid*, $O{<}^{CPh_2 \cdot C \cdot COOH}_{CO-CH}$, prepared by the action of hot water on β-bromo-γ-diphenylparaconic acid (*loc. cit.*), separates from water in crystals containing $1H_2O$, and melting at 100—$101°$; the anhydrous acid, obtained by recrystallisation from benzene or carbon bisulphide, melts at 138—$139°$. The *calcium* and *silver* salts are anhydrous, but the *barium* salt contains $2\frac{1}{2}H_2O$.

γ-Diphenylcrotonolactone, $^{CH \cdot CPh_2}_{CH-CO}{>}O$, formed on elimination of carbonic anhydride from the foregoing acid consequent on protracted treatment with boiling water, crystallises from light petroleum in large prisms and melts at 130—$131°$; it dissolves in hot sodium carbonate, and the solution reduces potassium permanganate. M. O. F.

Condensation of Acetophenone with Diethylic Succinate.
By HANS STOBBE (*Annalen*, 1899, **308**, 114—155. Compare Abstr., 1895, i, 142).—γ-Phenyl-γ-methylitaconic acid crystallises from chloroform in a network of plates belonging to the monoclinic system ; it melts and decomposes at $171°$ (compare *loc. cit.*). The acid is sparingly soluble in cold water and requires 580 parts of benzene at $17°$ to dissolve it. The *anhydride* crystallises from carbon bisulphide in needles or plates, and melts at $114°$. Oxidation with potassium permanganate in alkaline solution resolves γ-phenyl-γ-methylitaconic acid into acetophenone and formic, acetic, pyruvic, oxalic, and malonic acids.

γ-Phenyl-γ-methylpyrotartaric acid, $CHMePh \cdot CH(COOH) \cdot CH_2 \cdot COOH$, prepared by reducing γ-phenyl-γ-methylitaconic acid with sodium amalgam, crystallises from benzene and melts at 144—$146 \cdot 5°$; the *calcium* salt forms a gelatinous precipitate, and the *silver* salt resists the action of light.

cis-β-Bromo-γ-phenyl-γ-methylparaconic acid melts and decomposes at 161° (compare *loc. cit.*); boiling water converts it into γ-phenyl-γ-methylaconic acid, of which the *barium* salt is anhydrous.

γ-*Phenyl-γ-methylisoitaconic acid*, CMePh:C(COOH)·CH₂·COOH, produced along with the isomeride on condensing acetophenone with diethylic succinate, crystallises from ether in long needles, and melts at 183—185°, when it decomposes; it dissolves in 475 parts of water at 17°, and in 2000 parts of cold chloroform, but is virtually insoluble in benzene. The *calcium* salt contains 2H₂O, and the *barium* salt is anhydrous; the *diethylic* salt boils at 305—307°. The *anhydride* melts at 138°, and then becomes greenish-yellow; it separates in acetic chloride in monoclinic, hemimorphic crystals, and from chloroform and carbon bisulphide in rhombic plates. Phenylmethylisoitaconic acid gives rise to the same products of oxidation as the isomeride.

trans-β-*Bromo-γ-phenyl-γ-methylparaconic acid*,

$$\begin{array}{c}\text{CO—CH}_2\\ \text{O·CMePh}\end{array}\!\!\!\Big\rangle\text{CBr·COOH,}$$
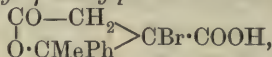
prepared by the action of bromine on phenylmethylisoitaconic acid, crystallises from benzene in aggregates of transparent prisms and melts at 129°, decomposing slowly at 147°.

[With Georg Heun.]—*Ethylic hydrogen-γ-phenyl-γ-methylisoitaconic acid*, CMePh:C(COOEt)·CH₂·COOH, dissolves in 200 parts of boiling water and crystallises in thin leaflets melting at 110—112°; on adding petroleum to the solution in benzene, it separates in long needles belonging to the rhombic system. The *calcium* and *barium* salts dissolve readily in water, the former containing 1H₂O; the *silver* salt crystallises from water in small prisms and becomes violet when exposed to light. Bromine converts the acid into the *ethylic* salt of *trans*-β-bromo-γ-phenyl-γ-methylparaconic acid, which separates from petroleum in rhombohedric crystals and melts at 103—104°.

γ-*Phenyl-γ-methylenepyrotartaric acid*,

$$\text{CH}_2\text{:CPh·CH(COOH)·CH}_2\text{·COOH,}$$
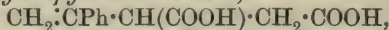
formerly described as phenylmethylaticonic acid (*loc. cit.*), melts at 152—154° without decomposing; it is more sparingly soluble in water than the isomeric itaconic acids, but in its solubility in ether it lies between phenylmethylitaconic acid and the isomeride, being six times more soluble than the latter. The *calcium* and *barium* salts are anhydrous. Oxidation converts a portion of the acid into β-benzoylpropionic and oxalic acids, and bromine gives rise to β-*bromo-β-phenyl-butyrolactoneacetic acid*, CH₂$\Big\langle\begin{array}{c}\text{CBrPh}\\ \text{O—CO}\end{array}\!\!\!\Big\rangle$CH·CH₂·COOH, which melts and decomposes at 177°; when the last-named substance is treated with boiling water, the *lactone* of β-hydroxy-β-phenylbutyrolactoneacetic acid, O$\Big\langle\begin{array}{c}\text{CH}_2\text{·CPh—O}\\ \text{CO—CH·CH}_2\end{array}\!\!\!\Big\rangle$CO, is produced, crystallising in long needles melting at 144°. M. O. F.

Condensation of Deoxybenzoin with Diethylic Succinate. By Hans Stobbe and Karl Russwurm (*Annalen*, 1899, **308**, 156—174). —γ-*Phenyl-γ-benzylidenepyrotartaric acid*,

$$\text{CHPh:CPh·CH(COOH)·CH}_2\text{·COOH,}$$
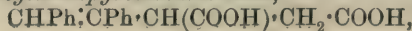
prepared from deoxybenzoin and diethylic succinate, crystallises from dilute aqueous solution in leaflets and melts at 151—152° without decomposing ; it separates from benzene in flat needles containing 1 mol. of the solvent.   The *barium* salt contains $3H_2O$, the *calcium* and *silver* salts being anhydrous ; the *diethylic* salt melts at 39—41° and boils at 230—240°.   Oxidation with alkaline potassium permanganate resolves the acid into benzaldehyde and benzoylpropionic acid, along with an acid, $C_{18}H_{14}O_5$, which melts at 203—204°.

β-Bromo-βγ-diphenylbutyrolactoneacetic acid,

$$CHPh{<}^{CPhBr}_{O-CO}{>}CH\cdot CH_2\cdot COOH,$$
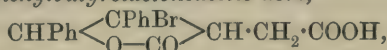
obtained by the action of bromine on γ-phenyl-γ-benzylidenepyrotartaric acid, crystallises from chloroform in white, lustrous leaflets, and melts at 144—145°, evolving hydrogen bromide.   Hot water converts the lactonic acid into the dilactone, $\overset{\displaystyle CHPh\cdot CPh-O}{\underset{\displaystyle O\cdot CO\cdot CH\cdot CH_2}{}}{>}CO$, the *lactone* of β-hydroxy-βγ-diphenylbutyrolactoneacetic acid, which crystallises in long, slender needles and melts at 189—191° without decomposing.

Stable *βγ-diphenylcrotonolactoneacetic acid,* $\overset{\displaystyle CHPh\cdot CPh}{\underset{\displaystyle O\text{———}CO}{}}{>}C\cdot CH_2\cdot COOH,$

is also produced by the action of hot water and alkalis on diphenylbromobutyrolactoneacetic acid, and melts at 212—214°, when it becomes red and evolves gas ; the *calcium, barium,* and *silver* salts are anhydrous.

When crude β-bromo-βγ-diphenylbutyrolactoneacetic acid is recrystallised from chloroform, the mother liquor contains the lactonic *acid,* $C_{18}H_{14}O_4$, which melts at 95°, and separates from benzene in crystals containing 1 mol. or 1½ mols. of the solvent ; the *acid* $C_{18}H_{16}O_5$ is also present, melting at 169—171·5° and containing ½ mol. of benzene when crystallised from that medium.   M. O. F.

Condensation of Dibenzyl Ketone with Diethylic Succinate. By HANS STOBBE, KARL RUSSWURM, and JULIUS SCHULZ (*Annalen*, 1899, **308**, 175—183. Compare Abstr., 1896, i, 235).—*γ-Benzyl-γ-benzylidenepyrotartaric acid,* $CHPh{:}C(CH_2Ph)\cdot CH(COOH)\cdot CH_2\cdot COOH,$ melts at 146—147° ; the ethylic *barium* salt crystallises from water in aggregates of small needles, and the ethylic hydrogen salt (*loc. cit.*) obtained by condensing dibenzyl ketone with diethylic succinate, melts at 127·5—129°.   The *sodium, calcium, barium,* and *silver* salts are anhydrous.   Oxidation with alkaline potassium permanganate converts the acid into δ-phenyl-lævulic acid, and bromine gives rise to *β-Bromo-γ-phenyl-β-benzylbutyrolactoneacetic acid,*

$$CHPh{<}^{CBr(CH_2Ph)}_{O\text{———}CO}{>}CH\cdot CH_2\cdot COOH,$$
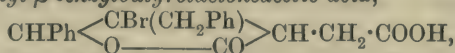
which melts at 157—159°, evolving gas.

γ-Phenyl-β-benzylcrotonolactoneacetic acid,

$$CHPh{<}^{C(CH_2Ph)}_{O\text{———}CO}{>}C\cdot CH_2\cdot COOH,$$
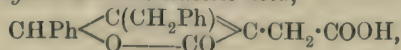
prepared by the action of a small quantity of hot water on the foregoing bromo-derivative, crystallises from a mixture of benzene and petroleum in needles, and melts at 115—117° ; the *calcium* and *silver*

salts are anhydrous. The *lactone* of β-hydroxy-γ-phenyl-β-benzyl-butyrolactoneacetic acid, $\begin{smallmatrix} \text{CHPh·C(CH}_2\text{Ph)·O} \\ | \qquad\qquad | \\ \text{O·CO·CH—CH}_2\text{—CO} \end{smallmatrix}$, crystallises from ether in slender needles, and melts at 202—203° without decomposing.

M. O. F.

Benzylidene Compounds of Hydroxy-Acids. By W. ALBERDA VAN EKENSTEIN and CORNELIS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1899, **18**, 305—308).—Idonic acid is readily separated from its stereoisomeride, gulonic acid, by treating a solution of their sodium salts with concentrated hydrochloric acid and benzaldehyde; the former acid alone combines with the aldehyde, yielding a dibenzylidene derivative insoluble in aqueous solutions. It was found that very few of the hydroxy-acids combine with benzaldehyde under these conditions; out of a total of 39, only three, namely, *l*-xylonic, *d*-saccharic, and *a*-glucoheptonic acids, yielded benzylidene derivatives; Some of the properties of these compounds are tabulated as follows:

Acids.	M. p.	$[a]_D$, 0·4 per cent. in methylic alcohol.	Solubility mgrm. per 10 c.c. at 17°.		
			Water.	Ethylic alcohol.	Methylic alcohol.
Dibenzylidene-*l*-idonic ...	215°	− 5°	25	30	35
Dibenzylidene-*l*-xylonic...	199	− 22	12	54	48
Benzylidene-*d*-saccharic...	215	+ 84	50	45	70
Benzylidene-*a*-gluco-heptonic...................	210	− 59	65	60	175

The number of benzylidene residues present in the condensation product is determined by heating the substance with dilute sulphuric acid and phenylhydrazine, and weighing the benzylidenephenylhydrazone produced; this process may also be applied to the proximate analysis of the benzylidene derivatives of hexahydric alcohols.

G. T. M.

Disulphones and Ketosulphones. By ELMER P. KOHLER and MARGARET B. MACDONALD (*Amer. Chem. J.*, 1899, **22**, 219—226).— Aromatic disulphones of the type $R·SO_2·SO_2R$ can be prepared by warming sulphonic chlorides with the sodium salt of a sulphinic acid, and sufficient water to form a paste. Ketosulphones are formed when an acidyl chloride is substituted in this reaction for the sulphonic chloride.

Diparatolyldisulphone, $S_2O_4(C_6H_4Me)_2$, prepared from paratoluenesulphonic chloride and sodium paratoluenesulphinate, is insoluble in water or alcohol, sparingly soluble in ether, and moderately soluble in chloroform or boiling benzene; it forms large, monoclinic tables, melts and decomposes at about 212°, and is not acted on by dilute acids and alkalis, although when heated with concentrated caustic potash it yields a mixture of potassium sulphonate and sulphinate.

Phenylparatolyldisulphone, $SO_2Ph \cdot SO_2 \cdot C_6H_4Me$, prepared from benzenesulphonic chloride and sodium paratoluenesulphinate, and also from paratoluenesulphonic chloride and sodium benzenesulphinate, crystallises in plates, melts at 166°, and, when heated with aqueous caustic potash, yields potassium benzenesulphonate and sulphinate and potassium paratoluenesulphonate and sulphinate.

Paratolylparanitrorthotolyldisulphone, $C_6H_4Me \cdot SO_2 \cdot SO_2 \cdot C_6H_3Me \cdot NO_2$, prepared from 3-nitrotoluene-6-sulphonic chloride and sodium paratoluenesulphinate, crystallises from chloroform in stout prisms, and melts at 154°; in its preparation diparatolyldisulphone is also formed, indicating that some of the chloride interacts with the sulphinate thus :

$$NO_2 \cdot C_7H_6 \cdot SO_2Cl + C_7H_7 \cdot SO_2Na = NO_2 \cdot C_7H_6 \cdot SO_2Na + C_7H_7 \cdot SO_2Cl.$$

Phenylparatolylketosulphone, $COPh \cdot SO_2 \cdot C_6H_4Me$, prepared by heating sodium paratoluenesulphinate and benzoic chloride dissolved in ether in a sealed tube at 110° for 72 hours, is a colourless oil which decomposes when distilled and solidifies when left in contact with aqueous sodium carbonate, yielding the *hydrate* $C_7H_7 \cdot SO_2 \cdot CPh(OH)_2$; this crystallises from light petroleum in stout needles and melts at 80°. Both the ketosulphone and its hydrate readily combine with hydrogen cyanide, hydroxylamine, phenylhydrazine, primary amines, and phenols, yielding crystalline products.   W. A. D.

Action of Sulphur Monochloride and Dichloride on Sulphinates, Thiosulphonates, and Mercaptans. By JULIUS TROEGER and VICTOR HORNUNG (*J. pr. Chem.*, 1899, [ii], **60**, 113—140). —*Benzenesulphonic bisulphide*, $(C_6H_5 \cdot SO_2)_2S_2$, prepared by the action of sulphur monochloride on sodium benzenesulphinate suspended in carbon tetrachloride, is a white, crystalline powder, and melts at 76—77°. The trisulphide (m. p. 103°) is the chief product when the action takes place in presence of water, or when the above mixture is not cooled sufficiently, and is also produced on attempting to recrystallise the bisulphide from hot alcohol. The action of sulphur monochloride on sodium paratoluenesulphinate gives as the chief product *paratoluenesulphonic bisulphide*, $(C_7H_7 \cdot SO_2)_2S_2$, a white powder melting at 98—100°, together with the monosulphide (Otto and Troeger, Abstr., 1891, 924), which crystallises from benzene in white needles and melts at 136°, and the *trisulphide*, which forms minute, white crystals and melts at 180°. The action of sulphur monochloride on sodium orthotoluenesulphinate gives only *orthotoluenesulphonic trisulphide*, $(C_7H_7 \cdot SO_2)_2S_3$, which crystallises from acetic acid in white, glistening needles and melts at 124—125°, and the bisulphide does not appear to be produced. Sodium α-naphthalenesulphinate similarly gives *α-naphthalenesulphonic trisulphide*, $(C_{10}H_7 \cdot SO_2)_2S_3$, a white, microcrystalline powder, which melts and chars at 167—168° and dissolves in benzene or ethylic acetate, but not in water or ether; *β-naphthalenesulphonic trisulphide* is a white, crystalline powder which melts and decomposes at 130—132°, dissolves readily in benzene or ethylic acetate, less readily in alcohol or chloroform, but not in water or light petroleum; the bisulphides could not be prepared.

The action of sulphur dichloride on sodium benzenesulphinate gives the monosulphide, $(C_6H_5 \cdot SO_2)_2S$, melting at 133°. *Paratoluenesulphonic sulphide*, $(C_7H_7 \cdot SO_2)_2S$, prepared similarly, crystallises from

glacial acetic acid in white needles, melts at 136°, dissolves readily in benzene or ethylic acetate, less readily in alcohol, but not in ether or water; it decomposes when kept. *Orthotoluenesulphonic sulphide* crystallises from acetic acid in white, glistening, monoclinic prisms, melts at 138—139°, and dissolves in benzene, alcohol, or chloroform, but not in water. *a-Naphthalenesulphonic sulphide*, $(C_{10}H_7 \cdot SO_2)_2S$, crystallises from acetic acid in glistening, pointed or columnar crystals, melts at 179—180°, dissolves readily in benzene or ethylic acetate, and slightly in alcohol, but not in water or ether. *β-Naphthalenesulphonic sulphide* crystallises from acetic acid in minute, white crystals, melts at 153°, dissolves readily in benzene, ethylic acetate, or chloroform, and slightly in alcohol, but not in water.

Benzenesulphonic tetrasulphide, $(C_6H_5 \cdot SO_2)_2S_4$, prepared by the action of sulphur monochloride on potassium benzenethiosulphonate, crystallises from acetic acid in minute, white crystals, melts at 84—85°, dissolves readily in benzene or ethylic acetate, and less readily in alcohol, but not in water. *Paratoluenesulphonic tetrasulphide*, $(C_7H_7 \cdot SO_2)_2S_4$, crystallises from acetic acid in white needles, melts at 108°, dissolves readily in benzene or ethylic acetate, and less readily in alcohol, but not in water. *Orthotoluenesulphonic tetrasulphide* was obtained as a pale yellow oil which did not crystallise. *a-Naphthalenesulphonic tetrasulphide*, $(C_{10}H_7 \cdot SO_2)S_4$, crystallises from acetic acid in white, microscopic crystals, melts at 148°, and dissolves in the ordinary solvents. *β-Naphthalenesulphonic tetrasulphide* crystallises from acetic acid as a white powder, melts at 90·—94°, and dissolves in the ordinary solvents.

The action of sulphur dichloride on potassium benzenethiosulphonate, potassium para- and ortho-toluenethiosulphonate, and potassium a- and β-naphthalenethiosulphonate, gave in each case the trisulphide already described.

Phenylic trisulphide, Ph_2S_3, prepared by the action of sulphur dichloride on phenylic mercaptan, is a golden-yellow, mobile oil, with a faint odour; it dissolves readily in benzene or ether, and less readily in alcohol, but not in water. *Paratolylic trisulphide* separates from alcohol as a white, crystalline powder, melts at 76—77°, and dissolves in benzene but not in water. *Orthotolylic trisulphide* was obtained as a yellow oil, heavier than water. *a-Naphthylic tetrasulphide*, $(C_{10}H_7)_2S_4$, prepared by the action of sulphur monochloride on a-naphthylic mercaptan, crystallises from acetic acid in fine-grained, yellow rhombohedra, melts at 102°, dissolves readily in benzene or ethylic acetate, and less readily in chloroform or light petroleum, but not in water. *a-Naphthylic trisulphide*, $(C_{10}H_7)_2S_3$, separates from acetic acid in pale yellow, microscopic crystals, and melts at 74—75°. *β-Naphthylic tetrasulphide* crystallises from acetic acid as a pale yellow powder, melts at 100—101°, and dissolves in the ordinary solvents. *β-Naphthylic trisulphide* separates from acetic acid as a fine, white, amorphous powder, melts at 108—109°, and dissolves in benzene or ethylic acetate, but not in water.

Amylic tetrasulphide, $(C_5H_{11})_2S_4$, prepared by the action of sulphur monochloride on amylic mercaptan, is a mobile, light yellow oil, soluble in benzene, ether, or alcohol, but insoluble in water. *Amylic*

trisulphide, $(C_5H_{11})_2S_3$, prepared by the action of sulphur dichloride on the mercaptan, is a golden-yellow, mobile oil of disagreeable odour, which dissolves in the ordinary solvents. T. M. L.

Action of Sulphonic Chlorides on the Metallic Derivatives of Ethereal Salts of Ketonic Acids. By ELMER P. KOHLER and MARGARET B. MACDONALD (*Amer. Chem. J.*, 1899, **22**, 227—239).— When paratoluenesulphonic chloride (1 mol.) is digested with ethylic sodacetoacetate ($1\frac{1}{2}$ mols.) in ethereal solution for 1 hour on the water-bath, the principal products are sodium paratoluenesulphinate and symmetrical diethylic diacetylsuccinate, but ethylic acetoacetate, chloracetoacetate, and paratoluenesulphonacetate,

$$C_6H_4Me\cdot SO_2\cdot CH_2\cdot COOEt,$$
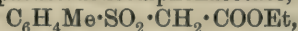
are also formed; it is probable that the first action is the formation of sodium paratoluenesulphinate and ethylic chloracetoacetate, a portion of the latter then interacting with unchanged ethylic sodacetoacetate to form diethylic diacetylsuccinate, whilst the remainder unites with the sodium paratoluenesulphinate, yielding ethylic acetate and paratoluenesulphonacetate. Ethylic chloracetoacetate, however, does not act on sodium paratoluenesulphinate dissolved in benzene or ether, but in presence of alcohol, ethylic acetate and paratoluenesulphonacetate are rapidly formed at the ordinary temperature; the action probably takes place in two stages: I. $CHClAc\cdot COOEt + C_6H_4Me\cdot SO_2Na = NaCl + C_6H_4Me\cdot SO_2\cdot CHAc\cdot COOEt$. II. $C_6H_4Me\cdot SO_2\cdot CHAc\cdot COOEt + EtOH = C_6H_4Me\cdot SO_2\cdot CH_2\cdot COOEt + CH_3\cdot COOEt$. When the mixture is warmed, the action takes place differently, the sulphinate being oxidised to sulphonate, whilst ethylic acetoacetate is formed.

The *ethylic paratoluenesulphonacetoacetate*, formed according to equation I, could not be isolated; the sodium derivative was obtained, however, in small amount, together with sodium paratoluenesulphinate, diethylic diacetylsuccinate, sodium mercaptide, and ethylic acetoacetate, on boiling an ethereal solution of equivalent quantities of ethylic sodacetoacetate and ethylic paratoluenethiosulphonate, $C_6H_4Me\cdot SO_2\cdot SEt$, for 30—40 hours, when it separated as a hard, granular deposit. It is rapidly decomposed by water into sodium acetate and ethylic paratoluenesulphonacetate, whilst the sodium derivative, $C_6H_4Me\cdot SO_2\cdot CHNa\cdot COOEt$, of the latter, together with ethylic acetate, are formed when it is treated with cold absolute alcohol; aqueous and alcoholic potash convert it into tolylmethylsulphone.

When a mixture of ethylic malonate, paratoluenesulphonic chloride, and sodium ethoxide in ethereal solution is heated on the water-bath for several hours, the principal products are ethylic ethylenetetracarboxylate and sodium paratoluenesulphinate; ethylic paratoluenesulphonosodacetate is also obtained, probably owing to the interaction of the paratoluenesulphinate with ethylic chloromalonate and subsequent hydrolysis of the *ethylic paratoluenesulphonomalonate*, $C_6H_4Me\cdot SO_2\cdot CH(COOEt)_2$, formed. This agrees with the fact that, when paratoluenesulphonic chloride is shaken with ethylic disodiomalonate in absolute alcohol, the *disodium* derivative,

$$C_6H_4Me\cdot SO_2\cdot CNa(COOEt)\cdot COONa,$$
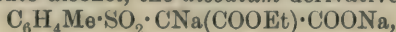
of monethylic paratoluenesulphonomalonate is obtained ; on acidifying
an aqueous solution of the latter with hydrochloric acid, carbonic
anhydride and ethylic paratoluenesulphonacetate are formed.

W. A. D.

Replacement of several Hydrogen Atoms in Benzene by
means of Mercury. By LEONE PESCI (*Real. Accad. dei Lincei*, 1899,
8, 130—133).—*Dimercuriobenzene acetate*, $C_6H_4Hg_2(OAc)_2$, obtained
by the action of mercury diphenyl on mercuric acetate, separates
from dilute acetic acid in the form of mammillary aggregates of
microscopic crystals which are insoluble in water, but dissolve in
boiling alcohol or benzene ; it decomposes without melting at about
230°. It is readily soluble in ammoniacal ammonium acetate solution,
giving a liquid from which it is precipitated unchanged by the addition
of acetic acid. Its solution yields, not mercury sulphide, but a white
precipitate when treated with hydrogen sulphide or alkali sulphides,
and it is completely soluble in sodium thiosulphate solution.

Dimercuriobenzene hydroxide, $C_6H_4Hg_2(OH)_2$, prepared by the action
of potassium hydroxide on the acetate, is a white powder composed of
mammiform, microscopic crystals which have an alkaline reaction and
are insoluble in the ordinary solvents. It deflagrates energetically at
a high temperature.

Trimercuriobenzene acetate, $C_6H_3Hg_3(OAc)_3$, obtained from mercury
diphenyl and mercuric acetate, forms a white precipitate composed of
very small mammillary crystals, and is insoluble in the ordinary
solvents, but dissolves slightly in boiling dilute acetic acid.   It
decomposes without melting at a high temperature, and with sodium
thiosulphate behaves like dimercuriobenzene acetate.

Trimercuriobenzene hydroxide, $C_6H_3Hg_3(OH)_3$, is a pulverulent sub-
stance consisting of very small crystals insoluble in the ordinary
solvents ; it does not melt, but at a high temperature decomposes with
intense deflagration.

Tetramercuriobenzene acetate, $C_6H_2Hg_4(OAc)_4$, is a white, powdery
product insoluble in the ordinary solvents ; on heating, it decomposes
without melting, and behaves like the preceding acetates with respect
to sodium thiosulphate.

Tetramercuriobenzene hydroxide, $C_6H_2Hg_4(OH)_4$, is a pale yellow,
amorphous powder which has an alkaline reaction, is insoluble in the
ordinary solvents, and deflagrates strongly at a high temperature.

T. H. P.

Action of Acetanilide on Mercuric Acetate. By LEONE PESCI
(*Chem. Zeit.*, 1899, 23, 58—59. Compare Abstr., 1895, i, 357, 358 ;
1898, i, 648).—2 : 4-*Dimercurioacetanilide acetate*,

$$NHAc \cdot C_6H_3(Hg \cdot OAc)_2,$$
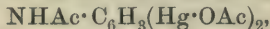
is formed when an intimate mixture of mercuric acetate (2 mols.) and
acetanilide (1 mol.) is heated at 114—115° until the mixture is com-
pletely fused, then kept at this temperature for 1 hour, and finally at
100° for 2 hours. If mixed while still hot with twice its volume of
hot water and then allowed to cool slowly, the acetate is obtained in
colourless tetrahedra melting at 220°. It usually separates from its

aqueous solutions as a gelatinous mass which slowly crystallises. The *hydroxide*, $NHAc \cdot C_6H_3(Hg \cdot OH)_2$, forms a white, insoluble powder decomposing above 280° without melting. The *sulphate*,

$$NHAc \cdot C_6H_3 \cdot Hg_2 \cdot SO_4,$$

crystallises in colourless needles, is insoluble in water or alcohol, but dissolves in warm, dilute acetic acid. J. J. S.

Electrolysis of Benzoin and of Benzil. By JOSEPH H. JAMES (*J. Amer. Chem. Soc.*, 1899, **21**, 889—910).—The electrolytic oxidation of benzoin in alcoholic sodium hydroxide gives the maximum yield of benzoic acid when a normal current density of 0·25 ampère is employed; with higher densities, less acid and more tarry matter are formed. In alcoholic sulphuric acid solution, a density of 0·5 ampère is required in order to bring about oxidation, the products being the same as in the alkaline solution. In alcoholic hydrogen chloride solution with a density of 1 ampère, the products are benzoic acid and benzil, but when currents of higher density are employed, benzil alone is formed.

The electrolytic reduction of benzoin in both alcoholic sulphuric acid and alcoholic hydrogen chloride solution gives rise to small quantities of a crystalline compound melting at 205—206°, the composition of which could not be determined. The oxidation of benzil in alcoholic sodium hydroxide solution yields no definite products, but in alcoholic sulphuric acid solution benzoic acid (14·5 per cent.) may be obtained; in hydrogen chloride solution no change takes place when a current of 1 ampère is employed, and on increasing the density to 7 ampères only tarry products are formed.

By the electrolytic reduction of benzil in alcoholic sulphuric acid, benzoin and a small amount of the substance melting at 205—206° are produced; benzoin is also formed when an alcoholic hydrogen chloride solution is employed, but no definite products can be isolated when the reduction takes place in alcoholic sodium hydroxide solution.

J. J. S.

Phenylhydrazones of Benzoin. By ALEXANDER SMITH (*Amer. Chem. J.*, 1899, **22**, 198—207).—The author confirms Smith and Ransome's statement (Abstr., 1894, i, 293), which Freer (*Amer. Chem. J.*, 1899, **21**, 14) has recently called in question, that benzoin-β-phenylhydrazone is converted into the α-compound when boiled with alcoholic phenylhydrazine. The "γ-phenylhydrazone," obtained by Freer (this vol., i, 357) by the action of benzoic chloride on an ethereal solution of the β-isomeride, is in reality benzanilide, ammonium chloride and benzil being also formed. Contrary to Freer's statement, the α-phenylhydrazone, when treated with benzoic chloride at the ordinary temperature, yields the same products as the β-compound, and when oxidised with nitrous anhydride gives rise to a considerable quantity of the red substance, melting at 137°, described by Freer as being formed only from the β-hydrazone. It thus appears either that both the phenylhydrazones of benzoin have the hydrazo-structure, or that, contrary to Freer's assumption, the formation of red compounds by the action of nitrous anhydride may occur in the case of true hydrazones.

W. A. D.

Preparation of Diphenylmethyleneaniline. By ERNEST NÄGELI (*Bull. Soc. Chim.*, 1899, [iii], **21**, 785—786).—Diphenylmethylene-aniline, $NPh{:}CPh_2$, is readily prepared by heating together benzo-phenone, aniline, and finely-powdered fused sodium sulphate for 18—20 hours at the boiling point of the mixture, and fractionally distilling the product. The yield is about 70 per cent. of the theoretical. N. L.

Action of Potassium Persulphate on Alkyl Groups. By C. MORITZ and RICHARD WOLFFENSTEIN (*Ber.*, 1899, **32**, 2531—2532. Compare this vol., i, 424).—*Diorthomethyldibenzyl,*

$$C_6H_4Me{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4Me,$$
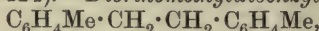
obtained by heating a mixture of orthoxylene and potassium per-sulphate at 100°, crystallises from alcohol in white, glistening needles and melts at 66·5°. *Diparamethyldibenzyl* forms white, glistening leaf-lets melting at 82°. *Symmetrical tetramethyldibenzyl,* $C_2H_4(C_6H_3Me_2)_2$, from mesitylene, melts at 77—78°. *Diethyldibenzyl,* $C_2H_2Et_2Ph_2$, from propylbenzene, forms white, talc-like leaflets and melts at 88°. *Di-metabutyldibenzyl,* $C_2H_4(C_6H_4{\cdot}CMe_3)_2$, from 1:3-tertiarybutyltoluene, crystallises in white leaflets and melts at 149°.

Besides the dibenzyl derivatives, metaxylene and metabutyltoluene yielded the corresponding aldehydes, which were identified by means of their hydrazones ; propylbenzene and the para- and meta-xylenes also gave benzoic and terephthalic or isophthalic acids respectively.

When acetic acid (50 grams) was heated on the water-bath for 8 hours with potassium persulphate (120 grams) and water (300 grams), it gave 0·8 gram of succinic acid. G. T. M.

Oxidation of Aldehydephenylhydrazones to α-Diketone-osazones. By HEINRICH BILTZ and ALBERT WIENANDS (*Annalen*, 1899, **308**, 1—17. Compare Biltz, this vol., i, 502).—*Cuminilosazone,* $C_2(C_6H_4Pr^\beta)_2(N_2HPh)_2$, prepared by passing air through a boiling solution of cumylidenephenylhydrazone in alcoholic potash, crystallises from alcohol in aggregates of pale yellow needles and melts at 253°, decomposing slightly ; when exposed to direct sunlight, it becomes bright red, regaining its yellow colour in the dark. The substance is identical with the osazone produced by the condensation of cuminil with phenylhydrazine, and probably represents the β-modification.
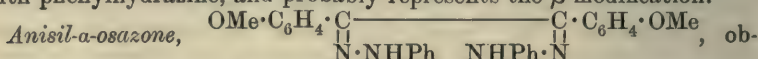
Anisil-α-osazone, $OMe{\cdot}C_6H_4{\cdot}\underset{N{\cdot}NHPh}{C}{-\!-\!-\!-}\underset{NHPh{\cdot}N}{C}{\cdot}C_6H_4{\cdot}OMe$, ob-

tained on oxidising anisylidenephenylhydrazone in very dilute alcoholic potash by air at 80°, crystallises from chloroform containing alcohol in small, pale yellow needles melting and decomposing at 171° ; it be-comes brownish-red when exposed to daylight, but is decolorised in the dark.

Anisil-β-osazone, $OMe{\cdot}C_6H_4{\cdot}\underset{NHPh{\cdot}N}{C}{-\!\!-}\underset{N{\cdot}NHPh}{C}{\cdot}C_6H_4{\cdot}OMe$, produced when a
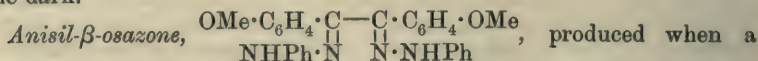
solution of the α-modification in glacial acetic acid is boiled in a reflux apparatus, separates in small, pale yellow crystals when hot water is added, and melts at 197° without decomposing ; it is also formed when anisil is heated with alcoholic phenylhydrazine hydrochloride.

Piperil-α-osazone, $CH_2O_2{:}C_6H_3{\cdot}C \underset{\underset{N{\cdot}NHPh}{\|}}{\qquad\qquad} \underset{\underset{NHPh{\cdot}N}{\|}}{C{\cdot}C_6H_3{:}CH_2O_2},$
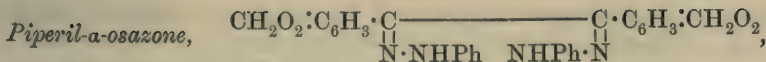
prepared by oxidising a boiling solution of piperonalphenylhydrazone in alcoholic potash, crystallises from a mixture of alcohol and benzene in microscopic needles, and melts at 183—184°, when it decomposes; it is sensitive to light, and forms a yellowish-brown solution in concentrated sulphuric acid.

Piperil-β-osazone, $CH_2O_2{:}C_6H_3{\cdot}\underset{\underset{NHPh{\cdot}N}{\|}}{C}{-}\underset{\underset{N{\cdot}NHPh}{\|}}{C}{\cdot}C_6H_3{:}CH_2O_2,$ obtained on
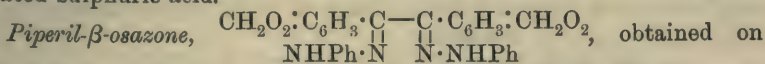
boiling a solution of the α-osazone in phenylhydrazine, crystallises in small, lemon-yellow needles and melts at 219—220°; it is identical with the osazone prepared from piperil.

Piperil, $C_2(C_6H_3{:}CH_2O_2)_2O_2$, produced when air is passed into a boiling solution of piperoin in aqueous potash during 4 hours, crystallises from a mixture of benzene and alcohol in pale yellow prisms, and melts at 171·5°. The *monoxime* melts at 199°, and yields an *acetate* melting at 124°; the *dioxime* crystallises from alcohol in lustrous prisms and melts at 244°, when it decomposes completely.

Vanillilosazone, $C_2[C_6H_3(OH)(OMe)]_2(N_2HPh)_2$, prepared by passing air through a solution of vanillinphenylhydrazone at the ordinary temperature, crystallises from ethylic acetoacetate containing alcohol in microscopic needles, and melts and decomposes at 199—200°; it resists the action of light, and has not been converted into an isomeric modification.

Japp and Klingemann (Trans., 1888, 519) observed the production of diacetylosazone when acetaldehydephenylhydrazone is heated above its melting point for a considerable period; the authors have obtained acetophenone from acetaldehydephenylhydrazone on oxidising the solution in alcoholic potash with air (compare von Pechmann, Abstr., 1898, i, 627). M. O. F.

Synthesis of Chrysin. By T. EMILEWICZ, STANISLAUS VON KOSTANECKI, and JOSEF TAMBOR (*Ber.*, 1899, **32**, 2448—2450).—Under the influence of metallic sodium, 2 : 4 : 6-trimethoxybenzoylacetophenone is produced from ethylic benzoate and the trimethylic ether of phloracetophenone, alcohol being eliminated; boiling hydriodic acid demethylates the product, forming chrysin, $C_6H_2(OH_2){<}^{O{-}CPh}_{CO{\cdot}CH} \underset{}{\overset{\|}{}}$.

2 : 4 : 6-*Trimethoxybenzoylacetophenone,* $C_6H_2(OMe)_3{\cdot}CO{\cdot}CH_2{\cdot}COPh$, crystallises from dilute alcohol in yellowish needles and melts at 100°; ferric chloride develops a red coloration with the alcoholic solution, and bromine in carbon bisulphide gives rise to a *bromo*-derivative, $C_{18}H_{17}O_5Br$, which crystallises in aggregates of needles and melts at 98—99°. M. O. F.

Alkyl Ethers of 3:3′:4′-Trihydroxybenzylidenecoumaranone. By STANISLAUS VON KOSTANECKI and A. RÓŻYCKI (*Ber.*, 1899, **32**, 2257—2260).—Emilewicz and von Kostanecki (this vol., i, 368), by condensing resacetophenone ethylic ether with piperonal, obtained 3-ethoxypiperonalcoumaranone, instead of the isomeric 3-ethoxy-3′ : 4′-methylenedioxyflavone, and it is now found that if methyl- and ethyl-

vanillin is substituted for piperonal, the reaction proceeds in a similar way.   2'-*Hydroxy*-4'-*ethoxy*-3 : 4-*dimethoxychalkone*,

$$OEt \cdot C_6H_3(OH) \cdot CO \cdot CH:CH \cdot C_6H_3(OMe)_2,$$
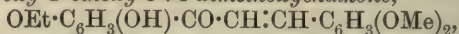
prepared from resacetophenone ethylic ether and methylvanillin in alcoholic sodium hydroxide solution, separates from alcohol or glacial acetic acid in yellow needles melting at 124—125°, which are coloured red by concentrated sulphuric acid, forming a yellow solution.   The *acetyl* derivative separates from alcohol in light yellow needles and melts at 106°, and its *dibromide*,

$$OEt \cdot C_6H_3(OAc) \cdot CO \cdot CHBr \cdot CHBr \cdot C_6H_3(OMe)_2,$$

forms a crystalline powder and melts with evolution of gas at 112—114°; when treated with alcoholic potassium hydroxide, this dibromide yields 3'-*ethoxy*-3 : 4-*dimethoxybenzylidenecoumaranone*,

$$OEt \cdot C_6H_3 {\displaystyle <^O_{CO}>} C:CH \cdot C_6H_3(OMe)_2,$$
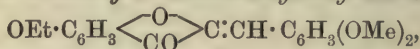
crystallising from alcohol in yellow needles melting at 148—149°, and forming a reddish-yellow solution in concentrated sulphuric acid ; when treated with an alcoholic solution of sodium ethoxide, it is transformed into a resin insoluble in alkalis.

   2'-*Hydroxy*-3-*methoxy*-4 : 4'-*diethoxychalkone*,

$$OEt \cdot C_6H_3(OH) \cdot CO \cdot CH:CH \cdot C_6H_3(OMe) \cdot OEt,$$
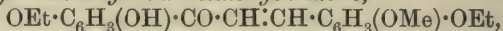
prepared from ethylvanillin and resacetophenone ethylic ether, separates from alcohol in small, broad, deep yellow prisms melting at 121—122°, which are coloured dark red by concentrated sulphuric acid and form an orange-coloured solution ; the *acetyl* compound separates from alcohol in light yellow needles melting at 103—104°, and its *dibromide* forms white, crystalline crusts melting at 107—108°. 3'-*Methoxy*-3 : 4'-*diethoxybenzylidenecoumaranone*,

$$OEt \cdot C_6H_3 {\displaystyle <^O_{CO}>} C:CH \cdot C_6H_3(OMe) \cdot OEt,$$

separates from alcohol in intensely yellow needles which melt at 133—135° and are coloured eosin-red by concentrated sulphuric acid.

                                                                              J. F. T.

   Condensation of Benzhydrols with Paraquinones and with Paraquinonoid Compounds.   By RICHARD MÖHLAU and VOLKMAR KLOPFER (*Ber.*, 1899, **32**, 2146—2159. Compare this vol., i, 62).—The condensation between alcohols and quinones only occurs when the alcohol is a true aromatic secondary alcohol and the quinone a paraquinonone or a derivative of the same.   The condensation takes place most readily in solution in absolute alcohol, or in a mixture of acetic and sulphuric acids, and, as a rule, an equal number of molecules of the constituents combine together, except in the case of quinone. The condensation products are well-defined, crystalline, coloured compounds ; when reduced, they yield quinols, but do not react with phenols, amines, or hydrazines in the same manner as the original quinones.

   Quinonebisdiphenylmethane, $C_6H_2O_2(CHPh_2)_2$ $[O_2:(CHPh_2)_2 = 1:4:2:5]$, obtained by heating an acetic acid solution of the constituents with 1 c.c. of sulphuric acid (1 : 19) for 12 hours on the water-bath, crystallises from alcohol in long, yellow, glistening prisms,

softening at 238° and melting at 250°. To obtain a satisfactory yield, it is essential that the materials should be pure. The product is soluble in benzene, sparingly so in alcohol or acetic acid, and insoluble in ether. When reduced, it yields *quinolbisdiphenylmethane*, $C_6H_2(CHPh_2)_2(OH)_2$, which crystallises from ether in prisms melting at 241° and is only sparingly soluble in alcohol. *Quinonebistetramethyldiamidodiphenylmethane*, $C_6H_2O_2[CH(C_6H_4 \cdot NMe_2)_2]_2$, obtained by heating the constituents in absolute alcoholic solution on the waterbath for 6 hours, crystallises from benzene in colourless crystals melting at 245°; on oxidation with potassium permanganate or lead peroxide, it turns bluish-green. The tetramethyldiamidobenzhydrol was obtained by reducing the corresponding ketone with hot amylic alcohol and sodium. *a-Naphthaquinonediphenylmethane*, $C_{10}H_5O_2 \cdot CHPh_2$, crystallises from alcohol in long, yellow, glistening, acicular prisms melting at 185°; it is sparingly soluble in acetic acid or alcohol, but dissolves more readily in ether, acetone, benzene, light petroleum, or ethylic acetate. When reduced, it yields *diphenyl-1 : 4-dihydroxynaphthylmethane*, $C_{10}H_5(OH)_2 \cdot CHPh_2$, which, however, could not be obtained in a crystalline form. *a-Naphthaquinonetetramethyldiamidodiphenylmethane*, $C_{10}H_5O_2 \cdot CH(C_6H_4 \cdot NMe_2)_2$, crystallises from ether in violet-red, glistening plates, which soften at 132° and melt at 152°; it is only sparingly soluble in alcohol or benzene, but dissolves readily in dilute acids; ammonium sulphide reduces it to the hydro-base, and lead peroxide and hydrochloric acid oxidise it to *a-naphthaquinonetetramethyldiamidodiphenylcarbinol*, the chloride of which combines with zinc chloride, yielding a dark blue powder having a constitution, $3C_{10}H_5O_2 \cdot C(C_6H_4 \cdot NMe_2) : C_6H_4 : NClMe_2 + 2ZnCl_2 + 2H_2O$, analogous to that of malachite-green. *3′ : 4′-Dihydroxy-a-naphthaquinonediphenylmethane*, $C_{10}H_3O_2(OH)_2 \cdot CHPh_2$, obtained by the condensation of alcoholic solutions of naphthazarin and diphenylcarbinol in the presence of a small quantity of sulphuric acid, crystallises from alcohol in golden-red needles melting at 196°, and is only sparingly soluble in alcohol or ether; when reduced with stannous chloride, it yields *1 : 4 : 3′ : 4′-tetrahydroxynaphthalenediphenylmethane*,

$$C_{10}H_3(OH)_4 \cdot CHPh_2,$$
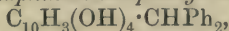
which crystallises in pale yellow, prismatic needles melting at 208° and only sparingly soluble in most solvents with the exception of benzene. *3′ : 4′-Dihydroxy-a-naphthaquinonetetramethyldiamidodiphenylmethane*, forms violet crystals melting at 183°, is moderately soluble in benzene, ether, or acetic acid, readily soluble in dilute acids, yielding ruby-red solutions, and sparingly in alkalis, giving blue solutions.

Paranitrosophenoltetramethyldiamidodiphenylmethane,

$$HO \cdot N : C_6H_3O \cdot CH(C_6H_4 \cdot NMe_2)_2,$$

obtained by boiling an alcoholic solution of paranitrosophenol and tetramethyldiamidobenzhydrol for 12 hours, crystallises from alcohol in yellow prisms melting at 217°; it is insoluble in alkalis, but dissolves readily in dilute acids.

When an alcoholic solution of paranitrosodimethylaniline and diphenylcarbinol is boiled for some hours, the product is Schraube's tetramethyldiamidoazoxybenzene (*Ber.*, 1875, **8**, 619; compare Pinnow and Pistor, Abstr., 1893, i, 509), and not, as expected, paranitrosodi-

methylanilidodiphenylmethane. *Paranitrosodimethylanilidotetramethyl-diamidodiphenylmethane*, $O<^{N}_{NMe_2}>C_6H_3 \cdot CH(C_6H_4NMe_2)_2$, crystallises from benzene in yellow, acicular prisms melting at 212°, and is readily soluble in alcohol or ether; when reduced, it yields *hexamethyl-tetramidotriphenylmethane*, $NH_2 \cdot C_6H_3(NMe_2) \cdot CH(C_6H_4 \cdot NMe_2)_2$, which crystallises from ether in glistening prisms melting at 171°, and is readily soluble in the ordinary solvents.

Only such quinonimido-dyes condense with benzhydrols as can be regarded as derivatives of paraquinonimide. Indamines and indophenols are incapable of condensation. *Tetramethyldiamidodiphenyl-methanedimethylnaphthaphenoxazimium chloride hydrochloride*,

$$NMe_2Cl\dot:C_6H_3<^{N}_{O}>C_{10}H_5 \cdot CH(C_6H_4 \cdot NMe_2) \cdot C_6H_4 \cdot NMe_2, HCl,$$ obtained from alcoholic solutions of the hydrochloride of Meldola's blue and tetramethyldiamidobenzhydrol, forms a bluish-violet powder soluble in alcohol but insoluble in ether. *Tetramethyldiamidodiphenylmethane-dimethylhydroxynaphthaphenoxazimium chloride hydrochloride*, obtained from muscarin and tetraphenyldiamidobenzhydrol, forms a dark blue powder with a bronzy lustre, and is soluble in water, yielding a pure blue solution.

Tetramethyldiamidodiphenylmethanedimethylamidohydroxyphenoxazone-carboxylic acid hydrochloride,

$$HCl,NMe_2 \cdot C_6H_3<^{N}_{O}>C_6O(OH)(COOH) \cdot CH(C_6H_4 \cdot NMe_2)_2, HCl,$$

obtained from gallocyanin hydrochloride and tetramethyldiamido-benzhydrol, forms a blue powder insoluble in ether but soluble in water, giving a bluish-violet solution, and in dilute acids, yielding a magenta red solution. **J. J. S.**

Condensation of Ethylic Phthalate with Ethylic Glutarate. By W. DIECKMANN (*Ber.*, 1899, **32**, 2227—2233).—Ethylic phthalate undergoes condensation with ethylic glutarate in presence of metallic sodium and a few drops of alcohol, yielding *ethylic* 1 : 5-*diketopheno-heptamethylene*-2 : 4-*dicarboxylate* (symmetrical ethylic phthalylglutar-ate), $C_6H_4<^{CO \cdot CH(COOEt)}_{CO \cdot CH(COOEt)}>CH_2$, which crystallises in colourless needles melting at 86—87°. It dissolves in dilute aqueous alkalis, but the solution gradually becomes reddish-yellow, and then yields a new acid which has not yet been examined.

When treated with dilute sulphuric acid, ethylic phthalylglutarate yields 1 : 5-*diketophenoheptamethylene*, $C_6H_4<^{CO \cdot CH_2}_{CO \cdot CH_2}>CH_2$, which crystallises in large prisms melting at 45—46°. The *dioxime* melts and decomposes at 245°, whilst the *diphenylhydrazone* melts at 190°. Ethylic β-phenylglutarate reacts with ethylic phthalate in a similar manner, forming 3-*phenyl*-1 : 5-*diketophenoheptamethylene*-2 : 4-*dicarb-oxylate* (symmetrical ethylic phthalyl-β-phenylglutarate),

$$C_6H_4<^{CO \cdot CH(COOEt)}_{CO \cdot CH(COOEt)}>CHPh,$$
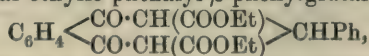
which crystallises in plates or prisms melting at 188°.

Ethylic suberate and ethylic sebacate, unlike the derivatives of glutaric acid, do not react in this manner.　　　　　　A. H.

Condensation of Benzil and Benzoin with Resorcinol. By HANS VON LIEBIG (*Ber.*, 1899, **32**, 2332—2335. Compare Japp and Meldrum, Trans., 1899, **75**, 1036).—By heating together benzil and resorcinol for 12 hours at 160°, a substance is produced to which the formula $C_2Ph_2\left(<^{C_6H_3(OH)}_{C_6H_3(OH)}>O\right)_2$ is assigned; it melts at 168°, crystallises from benzene in colourless, narrow, rhombic or needle-shaped plates, and from alcohol in characteristic, regular, four- or six-sided crystals whose corners are joined to the centre by radiating edges, the resulting triangles being striated parallel to the outer edges. Like fluorescein, it readily forms bromo- and nitro-derivatives; it dissolves readily in cold alcohol, ether, or acetone, and in hot benzene or chloroform, very slightly in water or light petroleum, and is soluble in concentrated sulphuric acid with a non-fluorescent, yellow to red colour; alkaline solutions become dark red on exposure to air, but without fluorescence; heating with zinc chloride does not convert the substance into a fluorescent compound. On heating with caustic soda and then acidifying, a crystalline substance, $C_{38}H_{26}O_6 + 11H_2O$, is precipitated, which is less soluble in alcohol or ether than the preceding compound and does not dissolve in benzene; it separates from alcohol in well-formed rhombohedra, effloresces in the air, and is converted on drying into the substance melting at 168°, of which it appears to be a hydrate (compare Hantzsch, this vol., i, 400).

The crude condensation product is always coloured red by a dye, $C_{38}H_{26}O_6 + 1\frac{1}{2}H_2O$, which forms the chief product if the condensation takes place in presence of zinc chloride; this separates on acidifying an alkaline solution as a dark-red, flocculent precipitate, melts at 114°, dissolves readily in ether, alcohol, or acetone with a green fluorescence, but only slightly in water, benzene, or petroleum, dissolves in caustic soda with a reddish-brown coloration, or in very dilute solution with a rose-red coloration and green fluorescence; it dyes animal fibres red to brown, whilst the nitro-derivative gives yellow to brown, and the bromo-derivative rose-red to red, shades. The acid liquors gradually deposit microscopic needles of a substance, $C_{38}H_{26}O_6 + 2H_2O$, which, when dried on the water-bath, gives the substance melting at 168°

A small quantity of a substance with an intense blue fluorescence was also isolated from the fusion of benzil and resorcinol with zinc chloride; it forms a brown, flocculent precipitate, and dissolves in caustic soda to a dark red solution with a splendid violet-blue fluorescence which gradually disappears, leaving a greenish brown-yellow solution; the solution in ammonia, on the other hand, gradually becomes intensely fluorescent.

By heating together benzoin and resorcinol for 6 hours at 180°, a substance was obtained to which the formula

$$OH·CHPh·CPh<^{C_6H_3(OH)}_{C_6H_3(OH)}>O$$
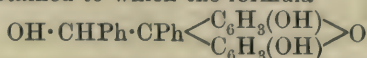
is assigned; it melts at 134°, crystallises from alcohol in dirty white

needles, dissolves readily in hot ether, benzene, acetone, or chloroform, very slightly in light petroleum or water, and gives a green to brown solution in sulphuric acid; it readily yields nitro- and bromo-derivatives, but does not give a fluorescent substance by fusion with zinc chloride. By the further action of caustic soda on the condensation product, a sodium salt was obtained which crystallised in flakes and showed a beautiful violet-blue shimmer; the corresponding phenol was obtained as a brown resin soluble in alcohol, ether, or benzene with a pale blue fluorescence, and separated from light petroleum in crystalline aggregates. A similar substance was obtained when zinc chloride was added to the mixture before fusion.   T. M. L.

New Method of Preparing Triphenyltrimesic Acid. By THEODOR LANSER (*Ber.*, 1899, **32**, 2478—2481).—An *anhydride*, $C_{27}H_{16}O_5$, of triphenyltrimesic acid is prepared by heating phenylpropiolic acid with phosphorus oxychloride at 90° until the evolution of hydrogen chloride ceases; when crystallised from a mixture of nitrobenzene and alcohol, it separates in colourless needles and melts at 256°; it is very insoluble in all organic solvents of low boiling point, but dissolves in cold alcoholic potash to form a potassium salt. 1 : 3 : 5-*Triphenyltrimesic acid*, $C_6Ph_3(COOH)_3$, obtained by dissolving the anhydride in hot aqueous potash and then acidifying the solution, crystallises from dilute alcohol and melts at 257—259° (compare Gabriel and Michael, Abstr., 1878, 734, who regarded the compound as phenenyltribenzoic acid, $C_6H_3(C_6H_4 \cdot COOH)_3$.

Trimethylic triphenyltrimesate, $C_6Ph_3(COOMe)_3$, crystallises from dilute alcohol in colourless leaflets and melts at 121°. The *triethylic* salt crystallises in colourless needles and melts at 129—130°.

Another *anhydride* of triphenyltrimesic acid, $C_6Ph_3:(CO \cdot O \cdot CO)_3:C_6Ph_3$, obtained by heating the acid to 200° or by treating it with phosphorus oxychloride, crystallises in needles and melts at 257—259°; it dissolves readily in benzene or in acetic acid and sparingly in alcohol.   G. T. M.

Nitration at Elevated Temperatures. By ERNEST NÄGELI (*Bull. Soc. Chim.*, 1899, [iii], **21**, 786—787).—Attempts to prepare β-nitronaphthalene by heating excess of naphthalene with potassium, or sodium, hydrogen sulphate, and potassium, or sodium, nitrate, at temperatures ranging from 150° to 360° were unsuccessful, the α-derivative alone being obtained, however the conditions are varied. When aniline is similarly treated, nitration occurs, but a large quantity of a bluishviolet substance is also formed. Benzoic acid and benzaldehyde are readily nitrated by heating with potassium hydrogen sulphate and potassium nitrate, the meta-derivative being in each case the principal product.   N. L.

Action of Diazonium Salts on Thymolsulphonic Acid. By JAMES H. STEBBINS, jun. (*J. Amer. Chem. Soc.*, 1899, **21**, 741—745. Compare Abstr., 1882, 834).—When a solution of diazonaphthionic acid is run into a well cooled alkaline solution of thymolparasulphonic acid, the colour changes to bright red and finally to a reddish-brown;

when allowed to remain overnight, then boiled and saturated with sodium chloride, a reddish-brown precipitate is deposited. The solution still contains a crimson-red dye which is extremely readily soluble in water, but is precipitated as its barium salt on the addition of barium chloride ; as the amount of the barium salt obtained was small, its constitution has not been determined. The brown precipitate yields a sparingly soluble *barium* salt, $BaC_{20}H_{18}S_2O_7N_2$, which crystallises from boiling water in orange-coloured, hair-like needles. The constitution of the brown dye is probably

$$SO_3H \cdot C_{10}H_6 \cdot N_2 \cdot C_6HMePr(OH) \cdot SO_3H \ [N_2 : Me : SO_3H : Pr : OH$$
$$= 1 : 2 : 3 : 5 : 6].$$
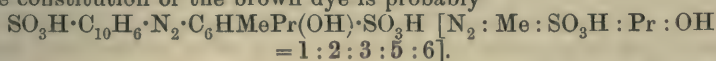
J. J. S.

Preparation and Properties of Naphthylcarbamides. By GEORGE YOUNG (*J. pr. Chem.*, 1899, [ii], 60, 255—256. Compare Trans., 1897, 71, 1200).—A claim for priority and a criticism of the work of Walther and Wlodkowski (this vol., i, 591). T. M. L.

Naphthylated Benzidines. By VICTOR MERZ and H. STRASSER (*J. pr. Chem.*, 1899, [ii], 60, 159—186).—α-*Naphthylbenzidine*,

$$NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH \cdot C_{10}H_7,$$
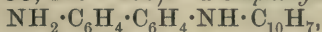
is prepared by heating α-naphthol with 1·1 to 1·4 mols. benzidine and a little calcium chloride in a stream of carbonic anhydride for 15—18 hours at a temperature rising gradually to 320°. After extracting the unchanged benzidine with much hot water, the α-naphthylbenzidine is partially separated from the α-dinaphthylbenzidine, which forms 20 per cent. of the crude product, by distilling in a current of superheated steam at 300—330°, or by distilling at 340—380° under 12—14 mm. pressure ; the separation is completed by converting the naphthylbenzidine into sulphate and extracting the dinaphthylbenzidine with benzene during 5 or 6 hours in a reflux apparatus ; the pure base is finally separated by redistilling, extracting with cold alcohol or ether, and crystallising from benzene. From benzene, it separates in colourless prisms, but from alcohol in glistening plates ; it dissolves only slightly in alcohol or ether, but readily in hot aniline, dissolves in 4—4½ parts of hot benzene and in 60 parts at 19°, with a faint bluish fluorescence. It melts at 154·5°, distils at 300—305° under 2—3 mm., at 355—360° under 11—12 mm., at 380—390° under 20—25 mm., and distils with partial decomposition at 500—505° under 755 mm. pressure. The *hydrochloride* and *sulphate* are insoluble and partially decomposed by boiling with water. A solution of the base in concentrated sulphuric acid gives a green coloration with sodium nitrite, whilst potassium nitrate gives an intense characteristic red-brown colour.

When 2 or 4 parts of α-naphthol are used for each part of benzidine, the product consisted chiefly of α-*dinaphthylbenzene*, the yields being 67 and 87 per cent. respectively, reckoned on the amount of benzidine used ; in the latter case, the excess of naphthol can be recovered by distillation. It crystallises from benzene in colourless, glistening needles, the solubility being 1 in 405 at 24° and 1 in 67·3 at the boiling point ; it is only very slightly soluble in alcohol and ether ; the solutions show a strong bluish-violet fluorescence, but become reddish to reddish-brown when exposed to air. It melts at 244·5 to 245°, and

boils at 380—390° under 3 mm. pressure, but is partially decomposed when distilled in a current of steam at 400°. A *hydrochloride* was obtained, but the base does not combine with sulphuric acid. A solution of the base in sulphuric acid is coloured dark green by sodium nitrite or potassium nitrate. A certain amount of α-naphthylene oxide is produced in the preparation of α-dinaphthylbenzidine.

β-Naphthylbenzidine, prepared and purified in a similar manner to the α-compound, than which it is less soluble, dissolves slightly in ether or in alcohol, and is soluble in 212 parts of benzene at 19°, the solution showing a bluish fluorescence; it crystallises in colourless, rhombic tablets, melts at 150—151°, but when crystallised from benzene becomes vitreous at 144—145°, and crystallises again before melting; it boils at 300—310° under 2—2·5 mm., at 370—373° under 12—13 mm., and distils with partial decomposition at 504—510° under 740 mm. pressure. The salts are sparingly soluble. The colour reactions are similar to those of α-naphthylbenzidine.

β-Dinaphthylbenzidine crystallises from much benzene in flakes, and from aniline in white, pearly, glistening plates; it dissolves in 307—309 parts of benzene at the boiling point, and in 5000—7000 parts at 20°, giving solutions with a bluish-violet fluorescence; it melts at 238·5—239° and boils at 370—380° under 2 to 2·5 mm. pressure; the solution in concentrated sulphuric acid shows a characteristic intense blue coloration with sodium nitrite or potassium nitrate.

αβ-Dinaphthylbenzidine, prepared by heating α-naphthylbenzidine with β-naphthol, or β-naphthylbenzidine with α-naphthol, melts at 200·5—201°, and boils at 365—375° under 2 mm. pressure; it is more soluble than the αα- and ββ-isomerides, dissolving in 201 parts of benzene at 24°, and in about 30 parts at the boiling point; it dissolves readily in hot aniline and very slightly in boiling alcohol or ether. The solutions in benzene show a violet fluorescence and become red on exposure to air; the solution in concentrated sulphuric acid is coloured green to bluish-black by nitrous and nitric acids. When heated with hydrochloric acid at 200°, the substance is decomposed into benzidine and α- and β-naphthol.   T. M. L.

The Ketones of Anthracene. By EDUARD LIPPMANN and FRANZ FLEISSNER (*Ber.*, 1899, **32**, 2249—2251).—*Benzoylanthracene* or *anthraphenone* is formed in small amount by the action of benzoic chloride on anthracene in presence of aluminium chloride, and crystallises in small needles melting at 138°. *Dibenzoylanthracene* is also formed in the reaction, and crystallises in yellow or brown needles melting above 300°.   A. H.

Action of Amines and of Amides on Acenaphthenequinone. By G. AMPOLA and V. RECCHI (*Real Accad. dei Linc.*, 1899, **8**, 209—218).—*Acenaphthenephenoparadiazine* (αα-naphthaquinoxaline), $C_{12}H_6 \ll^N_N > C_6H_4$, obtained by the interaction of molecular proportions of orthophenylenediamine hydrochloride and an acetic acid solution of acenaphthenequinone, is a white substance melting at 234° and subliming at a higher temperature in needles. It is soluble in the

ordinary solvents, from which it crystallises in slender needles arranged in glistening leaflets or small spheres. Cold chloroform dissolves it, as also do the concentrated mineral acids; with sulphuric acid, it gives a yellow, and with hydrochloric acid a red, solution and from both of these it is precipitated unchanged by the addition of water. The *hydrochloride*, $C_{18}H_{10}N_2,HCl$, is an intensely yellow substance which is readily decomposed by water and aqueous solvents; in the air, it loses hydrogen chloride and becomes heated. The *picrate*,

$$C_{18}H_{10}N_2,C_6H_3N_3O_7,$$
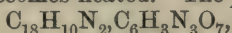
crystallises in long, yellow needles melting at 188°; it is slightly soluble in ether, more so in benzene or glacial acetic acid, but is decomposed by water. The *platinochloride*, $(C_{18}H_{10}N_2)_2,H_2PtCl_6$, separates from alcohol in very small, orange-yellow, glistening crystals which melt and decompose at a very high temperature; it is insoluble in benzene, ether, or acetic acid, and is decomposed by water with liberation of the base. On brominating the base, *dibromo-aa-naphtha-quinoxaline*, $C_{18}H_{10}N_2Br_2$, is obtained. It separates from glacial acetic acid solution in minute, glistening crystals which dissolve slightly in ether or chloroform; the bromine is removed, leaving the base, on either heating at 100°, or by treating with water, aqueous solvents, alkalis or zinc and acetic acid.

Dihydroacenaphtheneparadiazine, $C_{12}H_6 {\displaystyle \mathop{<\!\!\!<}} \begin{smallmatrix} N \cdot CH_2 \\ | \\ N \cdot CH_2 \end{smallmatrix}$, prepared from ethylenediamine and acenaphthenequinone, crystallises from dilute alcohol in long, slender, yellowish needles melting at 143°, and subliming at a higher temperature; it is insoluble in water or alkali solution, fairly soluble in mineral acids, and very soluble in alcohol, ether, or chloroform even in the cold. Its *picrate*, $C_{14}H_{10}N_2,C_6H_3N_3O_7$, crystallises from alcohol in beautiful, orange-yellow plates melting at 210°. The *platinochloride*, $(C_{14}H_{10}N_2)_2,H_2PtCl_6$, separates from acetic acid in small, yellow crystals which char without melting; it is fairly soluble in alcohol and is very readily decomposed by water. *Dibromodihydroacenaphtheneparadiazine*, $C_{14}H_{10}N_2Br_2$, separates from chloroform in yellow crystals which are soluble in alcohol or acetic acid and are decomposed by water, aqueous solvents, or alkalis, or by exposure to the air.

By the action of carbamide and fused sodium acetate on acenaphthenequinone, a *monourein*, $\begin{smallmatrix} CO \longrightarrow \\ | \\ C_{10}H_6 \end{smallmatrix} {>} C {<} \begin{smallmatrix} NH \\ \\ NH \end{smallmatrix} {>} CO$, is obtained which separates in sparkling white plates melting at 210°. It is insoluble in all the ordinary solvents, and when boiled with water is resolved into carbamide and acenaphthenequinone; it is not attacked by alkalis, but mineral acids and acetic acid decompose it with liberation of quinone. By the action of a large excess of carbamide on acenaphthenequinone, a *diurein*, $C_{12}H_6 {\left({<} \begin{smallmatrix} NH \\ NH \end{smallmatrix} {>} CO \right)}_2$, is formed. It is a reddish-brown substance which melts and decomposes at a high temperature and is insoluble in all ordinary solvents except acetic acid, which dissolves it slightly. To concentrated sulphuric acid it gives a red colour and to nitric acid a yellow colour; from both of these

solutions, water precipitates it unchanged. The *dinitrodiurein*, $C_{14}H_8N_6O_6$, is a yellow, crystalline powder fairly soluble in acetic acid or alcohol.   T. H. P.

Structure of Terpenes and Allied Compounds. XXIV. Limonene from Limonene Bromide. By J. GODLEWSKY and K. ROSHANOWITSCH (*Chem. Centr.*, 1899, i, 1241; from *J. Russ. Chem. Soc.*, 1899, **31**, 209—211).—Limonene bromide, melting at 104°, was prepared from carvene and then reduced in alcoholic solution with zinc dust. The limonene so obtained, after distilling in steam, drying over potassium carbonate, and distilling with sodium, boiled at 177·5° under 759 mm. pressure, had a sp. gr. 0·8585 at 0°/0°, 0·8441 at 20°/20°, 0·8584 at 0°/4°, 0·8425 at 20°/4°, and a specific rotatory power $[a]_D + 125°$ 36' at 20°. By the action of bromine, it forms the original bromide.   E. W. W.

Structure of Terpenes and Allied Compounds. XXV. Structure of Limonene. By J. GODLEWSKY (*Chem. Centr.*, 1899, i, 1241; from *J. Russ. Chem. Soc.*, 1899, **31**, 211—213).—When limonene free from carvone is oxidised by potassium permanganate, a small quantity of hydroxyterpenylic acid, $\begin{matrix} COO \cdot CMe \cdot CH_2 \cdot OH \\ | \qquad | \\ CH_2 - CH \cdot CH_2 \cdot COOH \end{matrix}$, is formed. This acid is identical with that obtained by oxidising carvone with potassium permanganate (Best, Abstr., 1894, i, 361), and melts at 174·5°. The dilactone of the acid melts at 129—130°, and when treated with potassium hydroxide regenerates hydroxyterpenylic acid.
                                        E. W. W.

Structure of Terpenes and Allied Compounds. XXII. Lævoterpene Hydrate. By J. GODLEWSKY (*Chem. Centr.*, 1899, i, 1241; from *J. Russ. Chem. Soc.*, 1899, **31**, 203—208.)—Lævoterpineol, $OH \cdot CMe_2 \cdot CH {<}^{CH_2 \cdot CH_2}_{CH_2 - CH}{>} CMe$, was prepared from turpentine by Flawitzky's method by means of alcoholic sulphuric acid, the mixture being shaken and the product poured into ice. In order to obtain a compound of high rotatory power, the reaction was only allowed to proceed for 10 hours. The terpineol obtained melts at 34°, and in alcoholic solution has a specific rotatory power $[a]_D - 95°$ 28' when $c = 21·4568$. By oxidising the terpineol with a 1 per cent. solution of potassium permanganate and then with chromic acid, the ketolactone,

$$\begin{matrix} O \cdot CMe_2 \\ | \qquad\quad {>} CH \cdot CH_2 \cdot CH_2 \cdot COMe, \\ CO \cdot CH_2 \end{matrix}$$
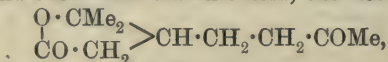
is formed. This compound, which was also prepared by oxidising menthanetriol (Ertschikowsky, *J. Russ. Chem. Soc.*, **28**, 132), when dissolved in alcohol, has a specific rotatory power $[a]_D + 55·3°$ if $c = 2·6187$. In the oxidation of lævoterpineol, active terpenylic acid, $\begin{matrix} O \cdot CMe_2 \\ | \qquad\quad {>} CH \cdot CH_2 \cdot COOH, \\ CO \cdot CH_2 \end{matrix}$ is also formed.   E. W. W.

Conversion of Geraniol into Terpineol (m. p. 35°). By KARL STEPHAN (*J. pr. Chem.*, 1899, [ii], **60**, 244—254. Compare this vol., i, 68).—When formic acid acts on geraniol at 0° to 5°, the chief product is geranyl formate, whilst on warming terpinene is formed; at a

temperature of 15° to 20°, however, the product consists largely of terpinyl formate. After the action had proceeded for 12 days, the product is hydrolysed, distilled in a current of steam, and fractionated under 13 mm. pressure ; the fraction of lowest boiling point had the characteristic odour of terpinene, but the nitrite could not be prepared ; 72 per cent. of the substance, however, distilled between 102° and 104° and solidified on cooling ; the crystals were drained and crystallised from light petroleum, and showed the normal density, melting point, boiling point, refractive index, and absence of rotatory power characteristic of cajeput oil. About 15 per cent. of the geraniol had been converted into terpineol.

Neither acetic acid nor acetic anhydride will convert geraniol into terpineol, but this change takes place rapidly on warming with acetic acid containing 1—2 per cent. of sulphuric acid, and more slowly, but with a better yield of terpineol, when the action takes place at the ordinary temperature.

For the separation of geraniol and terpineol, phthalic anhydride is used, which combines readily with the primary alcohols to form acid esters, but only slowly with secondary, and not at all with tertiary, alcohols ; after neutralising the solution with soda, the unchanged terpineol can be extracted with ether, whilst sodium geranyl phthalate remains behind, and can be hydrolysed with caustic alkalis.

The conversion of geraniol into terpineol is explained by the formation of an additive product with two molecules of acid, which are subsequently split off with formation of a ring-compound ; this intermediate product should be identical with that which is assumed to be formed in the conversion of linalool into terpineol, but it could not be isolated in either case.

By shaking with 5 per cent. sulphuric acid for 10 days and boiling the terpin hydrate formed with dilute sulphuric acid, geraniol can also be converted into a liquid terpineol identical with that prepared from pinene.

When steam is passed into an aqueous solution of sodium geranyl phthalate, there is produced, together with geraniol, a considerable amount of inactive linalool. This affords a third method of passing from geraniol to linalool (compare Tiemann, *Ber.*, 1898, **31**, 832, and Schimmel's *Berichte*, April 1898, 25). T. M. L.

Orientation in the Terpene Series : Exhaustive Bromination of Isogeraniolene and of Ionene. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1899, **32**, 2429—2447. Compare Abstr., 1898, i, 675).—It has been shown that when euterpene is submitted to the authors' process for converting monocyclic terpenes into the corresponding derivatives of benzene (*loc. cit.*), ethylxylene is produced, showing that bromination has not only removed hydrogen, but has also caused an atom of carbon to wander. Pursuing the line of inquiry suggested by this observation, the authors have obtained from isogeraniolene, $CMe_2 <^{CH_2 \cdot CHMe}_{CH_2——CH}> CH$, a mixture of the tetrabromides, $CMe <^{CMe \cdot C(CH_2Br)}_{CBr====CBr}> CBr$, and $CMe <^{CBr \cdot C(CH_2Br)}_{CMe——CBr}> CBr$, whilst

ionene, $\begin{array}{c} \text{CH=CH·CH·CMe}_2\text{·CH}_2 \\ \text{CMe:CH·CH——CH:CH} \end{array}$, yields the tetrabromide,

$$\begin{array}{c} \text{CH=CH—C·C(CH}_2\text{Br):CMe} \\ \text{CMe:CBr·C——CBr==CBr} \end{array}$$

The mixture of tetrabromides, prepared by saturating with hydrogen bromide a solution of isogeraniolene in glacial acetic acid, pouring the liquid on ice, and treating the hydrobromide thus obtained with bromine (10 parts) and iodine (0·1 part), crystallised from ethylic acetate in long needles, and melted somewhat indefinitely at 137—139°; the mixture of acetyl derivatives, obtained by the action of silver acetate, crystallised from dilute acetic acid in needles and leaflets, and yielded a mixture of alcohols, $C_9H_9OBr_3$, which crystallised from ethylic acetate in long prisms and melted at 227—228·5°. Reduction with sodium amalgam removed bromine from the mixed alcohols, converting them into an oil, which chromic acid oxidised to the aldehydes; the latter reduced potassium permanganate, yielding paraxylic, α-hemellithylic, and hemimellitic acids. It follows that a methyl of the *gem*-dimethyl group in geraniolene has occupied one of the two possible ortho-positions, giving rise to hemellithene, $\text{CMe}\!<\!\begin{array}{c}\text{CMe·CMe}\\\text{CH=CH}\end{array}\!>\!\text{CH}$, and pseudocumene.

1-*Bromomethyl*-2 : 3'-*dimethyl*-3 : 4 : 4'-*tribromonaphthalene*,

$$\begin{array}{c} \text{CH=CH—C·C(CH}_2\text{Br):CMe} \\ \text{CMe:CBr·C——CBr==CBr} \end{array},$$
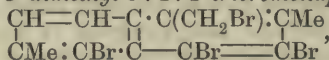
prepared from ionene hydrobromide and bromine with a small proportion of iodine, crystallises from xylene in flat prisms, and melts at 217—220°; when heated with nitrobenzene, glacial acetic acid, and silver acetate, it yields the *acetyl* derivative of 1-methylol-2 : 3'-dimethyltribromonaphthalene, which crystallises in long needles melting at 181—183°. 1-*Methylol*-2 : 3'-*dimethyltribromonaphthalene*, $C_{13}H_{11}OBr_3$, obtained on hydrolysing the acetyl derivative, melts at 230—231°; the *ethylic ether* crystallises from ethylic acetate, and melts at 141—142°. 1-*Methylal*-2 : 3'-*dimethyltribromonaphthalene*, $C_{13}H_9OBr_3$, formed on oxidising the alcohol with chromic acid, crystallises from benzene in needles and melts at 200—204°.

2 : 3'-*Dimethyltribromo-α-naphthoic acid*, $C_{13}H_9O_2Br_3$, prepared from the aldehyde by oxidation with nitric acid in nitrobenzene, melts at 244—245·5°; the *ethylic* salt crystallises in needles, and melts at 138—142°. 2 : 3'-*Dimethyl-α-naphthoic acid*, $C_{13}H_{12}O_2$, obtained on reducing the tribromo-derivative with sodium amalgam, crystallises from benzene in flat prisms, and melts at 168—171°. 2 : 3'-*Dimethylnaphthalene*, $C_{12}H_{12}$, formed on eliminating carbonic anhydride from the acid by means of hot lime, crystallises from alcohol in plates melting at 110—111°; the hydrocarbon is readily volatile in steam, and has a faint odour of orange-blossom. The *picrate* crystallises from alcohol in orange-yellow needles, and melts at 142—143°.

2 : 3'-*Dimethyl-α-naphthaquinone*, $C_{12}H_{10}O_2$, obtained by oxidising dimethyl-α-naphthoic acid with chromic acid, crystallises from ethylic acetate in yellow prisms, and melts at 137—138°; further oxidation with potassium permanganate converts the quinone into trimellitic acid.

1-*Methylol*-2 : 3′-*dimethylnaphthalene*, $C_{13}H_{14}O$, prepared from the acetyl derivative of the tribromo-compound by reduction with sodium amalgam, crystallises in long needles without a definite melting point ; the *picrate* forms orange-yellow needles melting somewhat indefinitely at 83°. 1-*Bromomethyl*-2 : 3′-*dimethylnaphthalene*, obtained by the action of hydrobromic acid on the foregoing alcohol, crystallises in leaflets, and melts at 107—108·5°. Reduction with zinc dust and alcoholic hydrochloric acid converts it into 1 : 2 : 3′-*trimethylnaphthalene*, $C_{13}H_{14}$, which boils at 154—156° under 15 mm. pressure ; the *picrate* melts at 122—123°.　　　　　　　　　　　　　　　　　　　　　M. O. F.

Ethereal Oils. By SCHIMMEL AND Co. (*Chem. Centr.*, 1899, i, 1042—1043 ; from *Geschäftsber.*, April 1899).—Cananga oil, from Samarang in Java, is distilled from the green leaves and has practically the same physical constants as the other varieties of the oil. It is insoluble in 10 volumes of 95 per cent. alcohol, has a sp. gr. 0·930 at 15°, rotatory power – 19° 21′, and saponification number 24·34. The oil obtained from the yellow leaves has a sp. gr. 0·956 at 15°, rotatory power – 25° 11′, is insoluble in 10 volumes of 95 per cent. alcohol, and contains about 12 per cent. of eugenol. The odour of this oil is inferior to that of the Manilla oil.

Cognac oil has a sp. gr. 0·878—0·880 at 15°, rotatory power – 0° 3′—0° 11′, acid number 50·9—68·6, ether number 140·9—218·6 and is soluble in two or more volumes of 80 per cent. alcohol. A higher sp. gr. or a higher ether number indicates the presence of artificial cognac oil.

The eucalyptus oil from *Eucalyptus macrorrhyncha*, which yields 0·287 per cent., is a reddish-brown liquid with a pleasant odour, has a sp. gr. 0·927 at 18° and contains 53·2 per cent. of cineol, traces of phellandrene, and considerable quantities of eudesmol (Baker and Smith, *Proc. Roy. Soc. New South Wales*, 1898, **32**, 104). *Eucalyptus capitellata* yields 0·103 per cent. of a dark red oil which has a sp. gr. 0·9153 at 18° and contains 38·4 per cent. of cineol, traces of phellandrene, and a small quantity of eudesmol. *Eucalyptus eugenioïdes* yields 0·689—0·795 per cent. of a colourless oil with a pleasant odour ; it has a sp. gr. 0·907—0·908 at 22°, specific rotatory power $[a]_D + 3·745 + 5·246°$, and contains 28·4—31·4 per cent. of cineol. *Eucalyptus dextropinea* yields 0·825—0·850 of an oil of sp. gr. 0·8743—0·8763 at 17° and *Eucalyptus lævopinea* 0·66 per cent. of an oil of sp. gr. 0·8732. The latter contains a large quantity of pinene (Baker, *Proc. R. Linn. Soc. New South Wales*, **26**, 414), which has hitherto only been found in small quantities in oils of the globulus class. The authors do not approve of Baker's designation of the dextro- and lævo-pinenes obtained from these oils as eucalyptene and eudesmene respectively.

Heracleum oil, prepared by distilling the fruit of *Heracleum sphondylium*, contains octylic alcohol. Octaldehyde, obtained by oxidising the alcohol, boils at 60—63° under 10 mm. pressure, and has a sp. gr. 0·827 at 15°. By the action of β-naphthylamine and pyruvic acid on octylic alcohol, *octyl-β-naphthacinchonic acid* is formed ; it separates in white crystals and melts at 234°. By the action of phosphonium iodide on octylic alcohol, a *compound* which melts at 115·5° is obtained.

Jasmine oil contains benzylic acetate, linalylic acetate, and benzylic alcohol, but not phenylglycolmethyleneacetal. Jaborandi leaf oil contains an unsaturated hydrocarbon which melts at 28—29°.

Rosewood oil, obtained by distilling the wood of *Convolvulus scoparius*, has a sp. gr. 0·951 at 15°, rotatory power +1° 30′, saponification number 0 and dissolves in 10 volumes of 95 per cent. alcohol. The saponification number of the acetyl derivative is 151·3.

From East Indian sandalwood oil, 85 per cent. of santalol may be isolated by means of phthalic anhydride. Santalol is a mixture of two sesquiterpene alcohols, of which the one of lower boiling point is inactive or dextrorotatory, whilst the other has a rotatory power −32° 36′ and a sp. gr. 0·979 at 15°. Santalylphthalic acid could not be obtained in a crystalline form, but silver santalylphthalate melts at 50°.

The melting point of the nitrosochloride prepared from oil of thyme gives no indication of the presence or absence of pinene as Labbé supposes (this vol., i, 621), trustworthy evidence only being obtained by preparing derivatives of the chloride.

Vetiver oil contains palmitic acid.

The ethereal oil prepared from the roots of *Alpinia malaccensis*, which yields 25 per cent. is, according, to van Romburgh, a colourless oil which has a pleasant odour, a sp. gr. 1·039—1·047 at 27°, a rotatory power +0° 25′ to +1° 5′ (20 mm. tube) and solidifies on cooling with separation of methylic cinnamate.   E. W. W.

Constituents of East Indian Sandalwood Oil. By Hugo von Soden and Fr. Müller (*Chem. Centr.*, 1899, i, 1082; from *Pharm. Zeit.*, **44**, 258—269).—Sandalwood oil has been stated to consist mainly of santalol, a sesquiterpene alcohol, $C_{15}H_{25} \cdot OH$, boiling at above 300°. Santalol contains, however, at least two different alcohols, of which the one of lower boiling point is slightly lævorotatory or inactive whilst the other has a rotatory power of about −20° to −30°. The mixture boils at about 303—306°, and both alcohols have the same specific gravity. Heine and Co.'s gonorol is prepared from the mixture by hydrolysing and fractionating in a vacuum. A sesquiterpene, *santalene*, $C_{15}H_{24}$, prepared by hydrolysing and then fractionating the oil, is a thin, colourless oil which has the odour of cedar, boils at 261—262°, has a sp. gr. 0·898 at 15°, a rotatory power of about −21°, is soluble in 16 parts of 90 per cent. alcohol, and is easily so in chloroform, ether, benzene, or light petroleum. It combines with hydrogen chloride or bromide (2 mols.) to form volatile additive products, and when treated with glacial acetic acid or sulphuric acid and a small quantity of water, yields a liquid which is probably the sesquiterpene alcohol, $C_{15}H_{26}O$; this has a stong, cedar-like odour, boils at 160—165° under 6 mm. pressure, and has a sp. gr. 0·978 at 15°.

Sandalwood oil also contains small quantities of phenols, lactones, and borneol (?). An acid which melts at about 154° was also isolated.
                                                                E. W. W.

Isolauronolic Acid : Constitution of Camphoric Acid, Camphor, and its Derivatives. By G. Blanc (*Ann. Chim. Phys.*, 1899, [vi], **18**, 181—288. Compare this vol., i, 630).—An exhaustive criticism of the formulæ for camphoric acid advocated by Bredt, Tiemann, and Bouveault leads the author to support that of the

last-named investigator; this expression, $CH_2 \Big\langle {}^{CMe_2 \cdot CMe \cdot COOH}_{CH_2 - CH \cdot COOH}$, although known as Bouveault's formula, was first suggested by W. H. Perkin, jun. (*Proc.*, 1896, **12**, 191), but has since been abandoned by that author in favour of the formula $\begin{smallmatrix} CH_2 \cdot CMe_2 - CMe \cdot COOH \\ CH(COOH) \cdot CH_2 \end{smallmatrix}$ (*Trans.*, 1898, **73**, 796). Isolauronolic acid, or *trimethyl*-1 : 1 : 2-*cyclopentene-*Δ^2-*methyloic*-3 *acid*, has the formula $CMe_2 \Big\langle {}^{CMe \cdot C \cdot COOH}_{CH_2 \cdot CH_2}$, whilst camphor is represented by the expression $CH_2 \Big\langle {}^{CMe_2 \cdot CMe \cdot CO}_{CH_2 - CH - CH_2}$.

The paper deals with practical details relating to the preparation of isolauronolic acid and its derivatives; many of these compounds have been already described (Blanc, Abstr., 1897, i, 201, 538, and 554), but the following substances are mentioned for the first time.

Isolauronolic aldehyde, $C_8H_{13} \cdot CHO$, prepared by distilling a mixture of calcium isolauronolate and calcium formate, is a colourless, mobile liquid having an agreeable, penetrating odour; it boils at 170° under 760 mm. pressure, and its sp. gr. is 0·8930 at 15°. The aldehyde gives Schiff's reaction, and reduces ammoniacal silver nitrate; the compound with sodium hydrogen sulphite dissolves very freely in water. The *semicarbazone* melts and decomposes at 212°, and the *semioxamazone* at 235°. The *cinchonic acid*, prepared by heating the aldehyde with β-naphthylamine and pyruvic acid, crystallises in yellow leaflets and melts at 257°.

The *ammonium*, *strontium*, *magnesium*, *manganese*, and *cadmium* salts of isolauronolic acid are crystalline, and the *ferric* salt, which is insoluble in water and alcohol, crystallises from ether; the *amylic* salt, boiling at 260°, has a sp. gr. 0·9378 at 15°, and the *phenylic*, *a-naphthylic*, and *β-naphthylic ethers* melt at 24·5°, 82°, and 82° respectively. The *anhydride* is a viscous liquid which boils at 210—215° under 13 mm. pressure, and has a sp. gr. 1·0287 at 15°. Both the *orthotoluidide* and *paratoluidide* melt at 114°, and the *a-naphthalide* and *β-naphthalide* at 148—149°.

Isolauronolic alcohol, $C_8H_{13} \cdot CH_2 \cdot OH$, obtained on reducing the aldehyde or the chloride, has a camphor-like odour, boils at 197° under 760 mm. pressure, and has a sp. gr. 0·9023 at 15°; the *acetyl* derivative boils at 209—210°.

The *base*, $C_8H_{13} \cdot CHMe \cdot NH_2$, prepared by reducing isolauronyl methyl ketoxime (Abstr., 1897, i, 554) with sodium in alcohol, boils at 190° under 760 mm. pressure, and has a sp. gr. 0·9558 at 15°; the *hydrochloride* crystallises in small prisms which melt and decompose at 230°, and the *platinochloride* is an orange, crystalline powder. The semicarbazone of isolauronyl methyl ketone melts and decomposes at 232—233°; on one occasion, a specimen melting at 49° was obtained (compare *loc. cit.*). M. O. F.

Constitution of Camphoric Acid. By G. BLANC (*Bull. Soc. Chim.*, 1899, [iii], **21**, 830—854. Compare this vol., i, 536 and 630).
—The comparative merits of the formulæ $CH_2 \Big\langle {}^{CMe_2 \cdot CMe \cdot COOH}_{CH_2 - CH \cdot COOH}$

(Bouveault, Blanc, compare preceding abstract) and

$$CH_2 \cdot CMe_2 \cdot CMe \cdot COOH$$
$$CH(COOH)CH_2$$
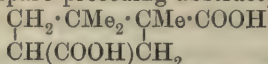
(Perkin, Trans., 1898, **73**, 796), for camphoric acid are considered in the present paper.

The author approaches the discussion by way of isolauronolic acid, and recalls the following facts as having led him to adopt for this compound the constitutional formula $CMe_2 \!\!<\!\! \begin{array}{c} CMe \vdots C \cdot COOH \\ CH_2 - CH_2 \end{array}$.

1. The acid is optically inactive. 2. Oxidation with nitric acid yields unsymmetrical αα-dimethylglutaric acid. 3. Oxidation with chromic acid yields dimethyl-3 : 3-hexanone-2-oic acid. 4. Isolaurolene, C_8H_{14}, obtained by heating isolauronolic acid in sealed tubes at 300°, also yields dimethylhexanonic acid when oxidised with potassium permanganate. 5. The ketone, $C_8H_{13} \cdot CO \cdot CH_3$, formed when acetic chloride acts on isolaurolene under the influence of aluminium chloride, is identical with the product of the action of zinc methyl on isolauronolic chloride.

It is next pointed out that the formula $CMe_2 \!\!<\!\! \begin{array}{c} CHMe \cdot CH \\ CH_2 - C \cdot COOH \end{array}$' by which Perkin represents isolauronolic acid, is reached by ascribing the constitution $\begin{array}{c} CMe_2 \cdot CMe \\ CH_2 - C(COOH) \end{array} \!\!>\!\! CO$ to isolauronic acid, which he regards as the immediate product of oxidation, this formula being based on the assumption that dihydroisolauronic acid, the product of reduction with sodium amalgam, is an alcohol-acid which does not form a lactone. Repetition of his own experiments and a study of isolauronic acid, however, have led the author to results which confirm his previous conclusions, but are antagonistic to those of Perkin.

In the first place, purified isolauronolic acid is optically inactive. It is dimorphous, being obtainable in hexagonal prisms and large, slender plates belonging to the monoclinic system, and in octahedra belonging to the orthorhombic system, all three varieties melting at 135°. If the anhydride of racemic camphoric acid is employed for its production instead of dextrocamphoric anhydride, the product is the same, and cannot be resolved into optically active components by crystallising the cinchonine salt. Moreover, according to the author's view of the structure of isolauronolic acid, the compound obtained by Bürcker from the action of camphoric anhydride on benzene in presence of aluminium chloride (Abstr., 1895, i, 108 ; 1896, i, 179), should be optically active, and this is the case.

Phenyldihydroisolauronolic acid, $CMe_2 \!\!<\!\! \begin{array}{c} CMePh \cdot CH \cdot COOH \\ CH_2 - CH_2 \end{array}$, crystallises in colourless needles from a mixture of alcohol and light petroleum, and melts at 142° (compare *loc. cit.*) ; a 5 per cent. solution in alcohol gives $a_D + 6° 56'$ at 20°. The methylic salt melts at 93—94°, and gives $a_D + 11° 53'$ at 24°, whilst the *isobutylic* salt melts at 71—72° and gives $a_D - 1° 30'$ at 23°. The *chloride* crystallises in white needles melting at about 60°, and is very readily soluble in neutral solvents ; moist air decomposes it, and when heated in a vacuum at about 150°,

it is resolved into hydrogen chloride, carbonic oxide, and the unsaturated *hydrocarbon* $C_{14}H_{18}$, a somewhat viscous liquid which boils at 195—200° under 40 mm. pressure.

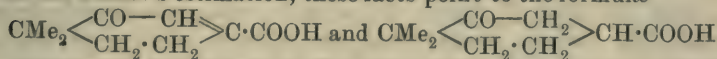When isolauronolic acid is oxidised with potassium permanganate at 0°, isolauronic acid is the main product, whilst oxalic, dimethylsuccinic, and dimethylhexanonic acids are formed in subordinate amount; if the operation is conducted at common temperatures, more than double the quantity of potassium permanganate is required, and the main products are oxalic and dimethylsuccinic acids, the amount of dimethylhexanonic and isolauronic acids being comparatively small. On oxidising the last-named substance with potassium permanganate at 15—20°, oxalic and dimethylsuccinic acids are produced, unaccompanied by a trace of dimethylhexanonic acid; according to Perkin (*loc. cit.*), this compound is formed when oxidation is effected by means of a mixture of chromic and sulphuric acids, but the quantity does not seem to be large. From these experiments, the author concludes that isolauronic acid is not the immediate result of oxidising isolauronolic acid, but represents a stage subsequent to the formation of dimethylhexanonic acid.

The final argument is based on the nature of dihydroisolauronic acid. As already stated, this compound is obtained on reducing isolauronic acid with sodium amalgam, and is regarded by Perkin as an

alcohol-acid, $\begin{array}{c} CMe_2 \cdot CMe \\ | \\ CH_2 - C(COOH) \end{array}$ >CH·OH, mainly on account of its inability to form a lactone. The author finds, however, that dihydroisolauronic acid is a ketone-acid, being not only indifferent towards acetic chloride, but capable of uniting with hydroxylamine and semicarbazide; the *oxime* and *semicarbazone* melt and decompose at 210° and 229° respectively. Dihydroisolauronic acid boils under the ordinary pressure without decomposition, and in consequence cannot have the ketonic group in the β-position with regard to carboxyl; it is therefore most probably a γ-ketone, and the γ-hydroxy-acid obtainable from it by reduction should be convertible into a lactone. This has been found to be the case. *Isolauronolide*, $C_9H_{14}O_2$, prepared by reducing dihydroisolauronic acid with sodium in absolute alcohol, has a faint odour of camphor, and melts at 53—54°; hydrolysis converts it into *tetrahydroisolauronic acid*, $C_9H_{16}O_3$, which crystallises from benzene in small prisms and melts at 142—143°.

In the author's estimation, these facts point to the formulæ

$$CMe_2 \begin{array}{c} <CO - CH \\ CH_2 \cdot CH_2 \end{array}> C \cdot COOH \quad \text{and} \quad CMe_2 \begin{array}{c} <CO - CH_2 \\ CH_2 \cdot CH_2 \end{array}> CH \cdot COOH$$

for isolauronic and dihydroisolauronic acids respectively. The expressions accord with the conversion of the latter into tetrahydroisolauronic acid, $CMe_2 \begin{array}{c} <CH(OH) \cdot CH_2 \\ CH_2 - CH_2 \end{array}> CH \cdot COOH$, and isolauronolide,
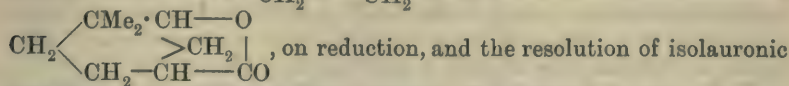
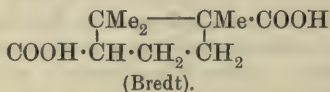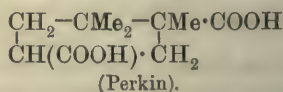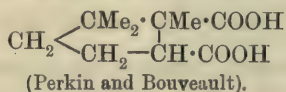$$CH_2 \begin{array}{c} <CMe_2 \cdot CH - O \\ CH_2 - CH - CO \end{array}> CH_2 \; | \quad , \text{ on reduction, and the resolution of isolauronic}$$

acid into aa-dimethylsuccinic and dimethylhexanonic acids by oxidation. They are easily reconciled also with the production of aromatic acids

from isolauronic acid under the influence of concentrated sulphuric acid and fused caustic potash. M. O. F.

Perkin's Constitutional Formula for Camphoric Acid. By G. BLANC (*Bull. Soc. Chim.*, 1899, [iii], **21**, 854—863. Compare foregoing abstract).—Whilst admitting that Perkin's formula explains the production of dimethylmalonic, trimethylsuccinic and camphoronic acids when camphoric acid is oxidised, the author points out that the formation of the acid $C_8H_{12}O_5$ along with oxalic acid, observed by Balbiano, is incompatible with it (compare this vol., i, 537). Proceeding to deduce from Perkin's formula constitutional expressions for important members of the isolauronolic and campholenic series, the author shows that conclusions to be drawn from this source are not easily reconciled with facts. M. O. F.

Constitution of Camphoric Acid. Synthesis of Ethylic Cyanodimethylcyclopentanone Carboxylate. By WILLIAM A. NOYES (*Ber.*, 1899, **32**, 2288—2292. Compare this vol., i, 284, 759).— Since the synthetical preparation of *i*-camphoronic acid has shown the presence of the group $\begin{array}{ccc} CMe_2 \cdot & CMe \cdot & C \\ | & | & | \\ C & C & C \end{array}$ in camphoric acid, the only formulæ containing a five-membered ring which are now admissible for this substance are those of

$$CH_2 \Big\langle \begin{array}{c} CMe_2 \cdot CMe \cdot COOH \\ | \\ CH_2 - CH \cdot COOH \end{array} \qquad \begin{array}{c} CH_2 - CMe_2 - CMe \cdot COOH \\ | \\ CH(COOH) \cdot CH_2 \end{array}$$

(Perkin and Bouveault). (Perkin).

$$\begin{array}{c} CMe_2 \overline{\qquad} CMe \cdot COOH \\ | \\ COOH \cdot CH \cdot CH_2 \cdot CH_2 \end{array}$$

(Bredt).

The second and third of these the author considers improbable from the fact that hydroxydihydrocampholytic acid does not yield a lactone when treated with dilute sulphuric acid, and therefore can hardly be a γ-hydroxy-acid, and that hydroxylauronic acid, not only does not yield a lactone, but on treatment with potassium dichromate and sulphuric acid loses carbonic anhydride and passes into a ketone, appearing therefore to be a β-hydroxy-acid. The second formula he considers inadmissible from the following facts.

[With J. W. SHEPHERD.]—*a-Hydroxydihydrociscampholytic acid*, obtained, in yield of about 10 per cent., when *a*-bromodihydro*cis*-campholytic acid is heated with an aqueous solution of barium hydroxide at 30—40°, crystallises from light petroleum or benzene in needles melting at 112°; when boiled with lead dioxide and dilute sulphuric acid, it is transformed into a *ketone*, $C_8H_{14}O$, which boils at 167—169° and has a sp. gr. 0·8956 at 20°/4°. These figures, although uncertain, owing to the small quantities of substance, seem to point to this compound being a derivative of cyclopentanone. The *oxime* crystallises from alcohol in needles and melts at 104°.

If the second formula for camphoric acid were correct, this ketone should condense with 2 mols. of benzaldehyde, but it is found to

combine with 1 mol. only, yielding a *condensation product* which crystallises from alcohol in colourless needles and melts at 74°.

The authors hope to effect the synthesis of this ketone in the following way : ethylic sodiocyanacetate combines with ethylic γ-bromisocaproate to form *ethylic cyanodimethylcyclopentanone carboxylate*, which crystallises from alcohol in needles melting at 148·5°, and according as alcohol is eliminated from one or other of the carbethoxy-groups, must have the constitution $CH_2 \begin{cases} CO-C(CN)\cdot COOEt \\ CH_2 \cdot CMe_2 \end{cases}$ or

$COOEt \cdot CH \begin{cases} CO-CH \cdot CN \\ CH_2 CMe_2 \end{cases}$.
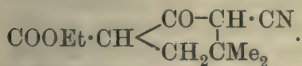
Ethylic γ-bromisocaproate combines in a similar way with ethylic sodioacetoacetate to form a colourless oil boiling at 180—190° under 30 mm. pressure, and with ethylic sodiomethylmalonate to form an oil boiling at 195—210° under 30 mm. pressure ; it is from the latter compound that it is hoped the 2 : 3 : 3-trimethylcyclopentanone, which is the constitution the author assigns to the ketone $C_8H_{14}O$, may be prepared.

The author considers that the formula $\begin{matrix} CH_2 \cdot CH \cdot CH_2 \cdot CH_2 \\ CO-CMe---CMe_2 \end{matrix}$ best expresses the constitution of camphor.   J. F. T.

The above formula for camphor has already been proposed by Bouveault (*Chem. Zeit.*, 1897, **21**, 762).   J. F. T.

Natural Resins [" Überwallungsharze "]. IV. Larch Resin. By MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1899, **20**, 647—659. Compare Abstr., 1898, i, 88).—Lariciresinol, after several recrystallisations from absolute alcohol and light petroleum or alcohol and water, forms white needles melting at 169°. It has the composition $C_{17}H_{12}(OMe)_2(OH)_4$, two of the hydroxyl groups being of a phenolic and two of an alcoholic character. The *tetracetyl* derivative crystallises from absolute alcohol in long needles, melts at 160°, and, on hydrolysis, yields a *substance*, $C_{19}H_{22}O_6$ (isomeric with lariciresinol), crystallising from alcohol in plates which melt at 97°. When the potassium derivative of lariciresinol is boiled with acetic anhydride, a *triacetyl* derivative is obtained ; this crystallises from alcohol in white needles, melts at 92°, and, when hydrolysed, gives the same substance as the tetracetyl derivative.

Diethyllariciresinol, $C_{17}H_{12}(OMe)_2(OEt)_2(OH)_2$, is prepared by treating an alcoholic solution of lariciresinol with potassium hydroxide and ethylic iodide. It forms white needles melting at 169°, and is insoluble in dilute potassium hydroxide. The *dimethyl* derivative is obtained similarly in the form of white needles which very quickly agglomerate.
       R. H. P.

Resin of Convolvulus Althæoides. By NICOLAS GEORGIADÈS (*J. Pharm.*, 1899, [vi], **10**, 117—119).—The roots of *Convolvulus althæoides* contain about 7 per cent. of a greenish-yellow resin which is insoluble in water. The resin is rendered partially soluble in water by the action of cold sulphuric, hydrochloric, or nitric acids, but no coloration is produced. It is decomposed by dilute acids, and a soluble

reducing substance is formed. It is therefore probably composed of glucosides. H. R. Le S.

Essential Oils and Glucosides of Cresses. By JOHANNES GADAMER (*Ber.*, 1899, **32**, 2335—2341. Compare Abstr., 1898, ii, 180, and Hofmann, Abstr., 1874, 792—793).—When prepared by steam distillation from the finely cut plants, the essential oils of *Tropæolum majus* and of *Lepidium sativum* consist principally of benzylthiocarbimide ; this is always mixed with benzylic cyanide, especially if the plants are only coarsely cut before the distillation. Both compounds are produced by the decomposition of a glucoside, the former by the action of the ferment myrosin, and the latter by the action of boiling water and acids. The glucoside could not be obtained in crystals, but when decomposed by silver nitrate gave an insoluble *silver* derivative, which dissolved at once in ammonia, separating again in a crystalline form with two molecules of ammonia ; to this compound the formula $CH_2Ph \cdot N \colon C(SAg) \cdot O \cdot SO_3Ag + 2NH_3$ is assigned, and the acid from which it is derived is named ' *tropæolic acid* ' ; the glucoside, to which the name of '*glucotropæolin*' is given, is regarded as having the constitution $CH_2Ph \cdot N \colon C(S \cdot C_6H_{11}O_5) \cdot O \cdot SO_3K + 2H_2O$.

The essential oil of *Nasturtium officinale* and *Barbarea præcox* consists chiefly of phenylethylenethiocarbimide, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot N \colon CS$, which was identified by converting it into the thiocarbamide ; as in the previous case, Hofmann, using the coarsely cut plants, obtained only the corresponding nitrile. The glucoside from which these are derived is named '*gluconasturtiin*,' and is regarded as having the constitution $CH_2Ph \cdot CH_2 \cdot N \colon C(S \cdot C_6H_{11}O_5) \cdot O \cdot SO_3K + xH_2O$, but could only be obtained as a syrup ; by decomposition with silver nitrate, it gives ' *silver nasturtiate*,' $CH_2Ph \cdot CH_2 \cdot N \colon C(SAg) \cdot O \cdot SO_3Ag + 2H_2O$, which also forms a crystalline compound with $2NH_3$, but loses this at ordinary temperatures.

When acted on by sodium thiosulphate, silver tropæolate and silver nasturtiate give a clear solution which probably contains the sodium salt, but soon decomposes into sodium sulphate and the thiocarbimide, which can then be extracted with ether. T. M. L.

Anemonin. By HANS MEYER (*Monatsh.*, 1899, **20**, 634—646. Compare Abstr., 1896, i, 623).—The hydroanemonin of Hanriot (*Bull. Soc. Chim.*, 1878, [ii], **47**, 683) is shown to be a mixture of *anemonolic acid* and its *diethylic* salt. This mixture is formed when anemonin is reduced with zinc and alcoholic hydrochloric acid, and from it the acid is obtained after hydrolysis with dilute aqueous hydrochloric acid, *Anemonolic acid*, $C_8H_{10}O_3(COOH)_2 + H_2O$, crystallises in the form of colourless tablets having a strong glassy lustre, and melts at 151—153°. It is dibasic, and forms soluble salts, with the exception of the *silver* salt, which is obtained as a bulky, white precipitate when silver nitrate is added to a neutralised solution of the acid. The *dimethylic* salt is formed when the silver salt is treated with methylic iodide, and also when anemonin dissolved in methylic alcohol is reduced by zinc and hydrochloric acid. It crystallises from ethylic acetate in large, lustrous tablets melting at 94—97°, and is very easily hydrolysed.

The paper concludes with a discussion of the formula of anemonin,

the author holding the view that this compound can form two classes of derivatives of the maleic and fumaric type. R. H. P.

Reaction of Santonin and the Desmotroposantonins with Ferric Chloride. By P. BERTOLO (*Gazzetta*, 1899, **29**, ii, 102—103). —The violet coloration produced when santonin is heated with dilute sulphuric acid and ferric chloride is also obtained with the desmotroposantonins and the santonous acids. The author is of opinion that for this coloration to be formed, it is necessary that the santonin derivative should contain either a phenolic hydroxy-group, or a carbonyl group capable of being transformed into a phenolic hydroxy-group.
T. H. P.

Resolution of Inactive Isosantonous Acid into its Dextro- and Lævo-components by means of Cinchonine. By AMERIGO ANDREOCCI and P. ALESSANDRELLO (*Gazzetta*, 1899, **29**, i, 479—483). —Isosantonous acid and cinchonine were dissolved in mol. proportions in 90 per cent. alcohol, and after adding a crystal of cinchonine dextrosantonate and allowing the liquid to evaporate, three crops of crystals and a syrupy residue were obtained. The first crystalline deposit was decomposed with dilute sulphuric acid and the liquid extracted with ether, the santonous acid thus obtained giving, after recrystallisation from alcohol, a specific rotatory power $[\alpha]_D + 73°$, and after again crystallising from alcohol a melting point of 178—179°; pure dextrosantonous acid has $[\alpha]_D + 74.8°$, and a melting point of 179—180°. On treating the residual syrup in a similar manner, it is found to consist almost entirely of the cinchonine salt of the lævo-acid, since, after crystallising from alcohol, the acid obtained has $[\alpha]_D - 74°$, and a melting point of 179—180°; for pure lævo-santonous acid, $[\alpha]_D - 74.4°$, and the melting point is 179—180°.

On partially saturating isosantonous acid with cinchonine, the proportions used being 2 mols. of the acid to 1 mol. of the base, a very good separation of the two isomerides is obtained, the salt of the dextro-acid separating first. T. H. P.

An Optically Active Partially Racemic Compound. By AMERIGO ANDREOCCI (*Gazzetta*, 1899, **29**, i, 513—516, and *Real. Accad. Linc.*, 1899, **8**, 80—86).—From dextro- and lævo-acetyldesmotroposantonin, the former melting at 156° and having a specific rotatory power $[\alpha]_D + 93.6°$, and the latter having a melting point 154° and an $[\alpha]_D - 119°$, by fusing them together and repeatedly crystallising the product from alcohol, or by simple crystallisation alone, a lævo-rotatory acetyl derivative is obtained which melts at 142° and has a specific rotatory power $[\alpha]_D - 12.8°$, which is the mean of those of the two components. Whilst the two components crystallise in slender prisms or needles, the double compound forms large, glistening prisms, and is much less soluble in acetic acid than its components. A dilute acetic acid solution of the double compound, when heated with a small quantity of sulphuric acid, gives rise to a mixture of the two desmotroposantonins, corresponding with the two original acetyl derivatives; from this mixture, the separate compounds are readily obtainable by crystallisation from alcohol or acetic acid. T. H. P.

Digitoxin and the Products of its Decomposition. By
HEINRICH KILIANI (*Arch. Pharm.*, 1899, **237**, 446—454, and *Ber.*, 1899,
32, 2196—2201 ; the two papers are largely identical. Compare this
vol., i, 70 ; and also Abstr., 1896, i, 59 ; 1897, i, 95).—When digitox-
ose, $C_6H_{12}O_4$, is oxidised with silver oxide and water, acetic acid is
one of the products ; hence digitoxose contains a CMe-group.

When digitoxigenin, $C_{22}H_{32}O_4$, is heated with 50 per cent. alcohol
and sodium hydroxide at 100°, crystals of *sodium dixgenate*,
$C_{22}H_{33}O_5Na + H_2O$, separate on cooling ; the corresponding acid,
dixgenic acid, $C_{22}H_{34}O_5$, melts at 220—230°.

Under similar circumstances, digitoxin, $C_{34}H_{54}O_{11}$, yields *sodium
digitoxate* ; the crystalline *calcium* salt, $(C_{34}H_{55}O_{12})_2Ca + 3H_2O$, cor-
responding with this was analysed. The calcium salt does not yield
digitoxin when treated with acetic acid.   C. F. B.

Digitalinum Verum and the Products of its Decomposition.
By HEINRICH KILIANI (*Arch. Pharm.*, 1899, **237**, 455—458, and *Ber.*,
1899, **32**, 2199 ; these are in part identical. Compare this vol., i, 71).
—By oxidising digitaligenin with chromic acid in acetic acid solution,
toxigenone is obtained, identical with that prepared in a similar
manner from anhydrodigitoxigenin.   C. F. B.

Digitalein. By HEINRICH KILIANI and ADOLF WINDAUS (*Arch.
Pharm.*, 1899, **237**, 458—466).—A digitalein in Schmiedeberg's sense
(compare Abstr., 1892, 1482), that is, a substance which is readily
soluble in water, and acts as a poison by paralysing the heart's action,
can be obtained from *Digitalis* seeds. The mother liquor of the digitalin
(Abstr., 1896, i, 52) is concentrated to a small bulk under diminished
pressure, and the residue saturated with ether to prevent the growth
of mould, and dialysed into water saturated with ether.

The dialysate is concentrated, extracted with ether to remove resin,
and precipitated with 10 per cent. tannic acid in slight excess only. The
precipitate is rubbed up with one-tenth of its weight of zinc oxide and
some water, the mixture then evaporated, and the residue extracted
with methylic alcohol. The ethereal extract is evaporated, and the
residue extracted with water saturated with ether, when some digi-
talin remains undissolved. The extract is evaporated, the residue
dissolved in alcohol (4 parts) and precipitated twice in succession
with ether (2 parts), after which the alcohol-ether is evaporated to
dryness. The residue of digitalein from 1 kilo. of *Dig. pur. pulv.*
weighed 4—5 grams ; a dose of 0·4 milligram produced permanent
systole in the frog.   C. F. B.

Digitogenin and its Derivatives. By HEINRICH KILIANI and
ADOLF WINDAUS (*Arch. Pharm.*, 1899, **237**, 466—471, and *Ber.*, 1899,
32, 2201—2205).—In consequence of Edinger's work (this vol., i, 377),
digitogenin and some of its derivatives (compare Abstr., 1891, 577 ;
1895, i, 65) have been analysed afresh. The results do not render it
possible to decide between $C_{30}H_{48}O_6$, $C_{30}H_{50}O_6$, and $C_{31}H_{52}O_6$ for the
formula of digitogenin ; that of digitogenic acid appears to be $C_{28}H_{44}O_8$;
a crystalline *cadmium* salt, $C_{28}H_{42}O_8Cd + H_2O$, of this acid was
analysed.

When digitogenic acid is heated for a short time at 160°, it yields

two products, namely, digitoic acid (Abstr., 1893, i, 666) and an isomeride of itself. This substance, $C_{28}H_{44}O_8$, is named *β-digitogenic acid* ; it differs from digitogenic acid in that it melts at 105°, and crystallises slowly from 50 per cent. alcohol in large, rather ill-defined prisms ; like its isomeride, it is dibasic, and forms a crystalline magnesium salt and an oxime.

Oxydigitogenic acid, $C_{28}H_{42}O_9$, now appears to be tribasic, and not dibasic. C. F. B.

A Compound of Glycuronic Acid with Parabromophenylhydrazine. By CARL NEUBERG (*Ber.*, 1899, **32**, 2395—2398).—If an aqueous solution of glycuronic acid is heated to boiling and treated with parabromophenylhydrazine acetate under certain conditions, a *compound* separates in bright, yellow needles, and may be purified by washing with water and absolute alcohol successively, and repeated crystallisation from 60 per cent. alcohol.

The new substance, whose exact nature has not yet been determined, has the composition, $C_{12}H_{17}O_7N_2Br$; it is sparingly soluble in hot water, benzene, ether, ethylic acetate, absolute alcohol, or amylic alcohol, insoluble in chloroform, somewhat readily soluble in hot glacial acetic acid and in 60 per cent. alcohol. Its alcoholic solution is strongly dextrorotatory. It is scarcely altered by boiling with baryta water or ammonia, and does not give Bülow's reaction for acid hydrazides ; the crystals, when moistened with alcohol, quickly redden magenta sulphurous acid. The cupric-reducing power is diminished after treatment with 1 per cent. alcoholic hydrogen chloride, a behaviour which might indicate that acetal formation had occurred. It appears to combine with hydroxylamine, but an oxime could not be isolated, and it was not found possible to obtain derivatives containing more hydrazine, owing to the formation of resinous products.

The application of the above observation to the detection of glycuronic acid in urine is being investigated ; it is to be noted that urochloralic acid yields the same compound after preliminary hydrolysis with dilute sulphuric acid. A. L.

Plumieride. By ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, **18**, 334—350).—The plumieride isolated by Boorsma from the bark of *Plumiera acutifolia* appears to be identical with the substance obtained by Merck (Abstr., 1897, i, 167) from the same source, although the former investigator stated that it did not melt, whereas the latter gave its melting point as 157—158°. The author finds that the substance melting at 157° is the hydrated form of plumieride ; when crystallised from dry ethylic acetate, it separates in the anhydrous condition, and then has no definite melting point. A molecular weight determination by the cryoscopic method gave numbers varying from 537 to 572 ; these values are approximately half those obtained by Merck, who used the ebullioscopic method. Plumieride is a glucoside, for when boiled with 5 per cent. hydrochloric acid it is hydrolysed, yielding glucose and an insoluble, amorphous, brown substance. An acid, for which the author proposes the name *plumieridic acid*, is produced by dissolving plumieride in aqueous potash and allowing the solution to remain for some time ; the solution, when acidified with

dilute sulphuric acid, yields the new compound, which is sparingly soluble in water. This acid is slightly soluble in methylic alcohol and insoluble in ethylic alcohol, ether, chloroform, or benzene; it decomposes at temperatures above 200°; its dilute aqueous solution is lævo-rotatory. The potassium salt crystallises from water. Plumieridic acid is also a glucoside, for on boiling with 5 per cent. hydrochloric acid it behaves like plumieride, yielding glucose and an amorphous, brown substance. Plumieride seems also to be identical with agoniadin, obtained by Peckolt (*Arch. Pharm.*, 1870, ii, 142, 40) from *P. lancifolia*, for the latter substance behaves similarly on hydrolysis and melts at 155°.   G. T. M.

2:2′:6:6′-Tetramethyldipyridyl and the Corresponding Tetra-carboxylic Acid. By FRANZ HUTH (*Ber.*, 1899, 32, 2209—2211. Compare Abstr., 1898, 687).—The gas evolved when 2:6-dimethyl-pyridine is heated with sodium consists of hydrogen and nitrogen, the former in larger amount.

The *hydrochloride, hydrobromide, hydriodide, nitrate*, and *silver nitrate* compound (with $1AgNO_3$) of the tetramethyldipyridyl are all un-melted at 260—280°; the nitrate crystallises with $1\frac{1}{2}H_2O$, and then melts at 145°.

The *calcium, barium*, and *copper* salts of the tetracarboxylic acid form insoluble precipitates; the first is crystalline in character.   C. F. B.

Picoline Haloids and Perhaloids. By PAUL MURRILL (*J. Amer. Chem. Soc.*, 1899, 21, 828—854. Compare Prescott, Abstr., 1896, i, 316; Prescott and Trowbridge, *ibid.*, i, 186).—*a*-Picoline methiodide melts at 224°, Ramsay (Abstr., 1879, 263) gives the melting point as 227°. The corresponding *β*- and *γ*-compounds have not been obtained in a pure form, but their melting points are apparently much lower than that of the *a*-compound. *a*-Picoline ethiodide crystallises in colourless, feathery plates melting at 123° (compare Anderson, *Phil. Mag.*, 1855, [iv], 9, 214). *Picoline propiodide* crystallises from alcohol in yellowish needles melting at 77°; the *isopropiodide* also crystallises in needles and melts at 142°; the *butiodide* forms straw-coloured crystals melting at 98°; the *isobutiodide* is a pale yellow syrup which does not solidify at $-15°$; the *secondary butiodide* is extremely unstable and could not be purified; picoline and tertiary butylic iodide, when heated at 100°, form picoline hydriodide and isobutylene. *Picoline isoamyliodide* forms straw-coloured, cubical crystals melting at 120°, and *picoline allyliodide* transparent, almost colourless cubes melting at 70° (compare Ramsay, *loc. cit.*). Picoline hydriodide forms a snow-white mass which is somewhat unstable, readily decomposing into the base and hydrogen iodide. *Picoline hydrogen di-iodide*, C_6H_7N,HI,I, obtained by adding an alcoholic solution of iodine (1 equiv.) to an alcoholic solution of the hydriodide, forms dark brown prisms melting not very sharply at 95°. Like the other periodides, it is much more stable than the simple hydriodide, and, like them, it liquefies on contact with water. The *tri-iodide*, C_6H_7N,HI,I_2, forms dark brown octahedra melting at 44°; the *pentiodide*, C_6H_7N,HI,I_4, is obtained as a thick, greenish-black oil which does not solidify at $-25°$.

a-*Picoline methyl tri-iodide*, C_6H_7N,MeI,I_2, forms bluish-black,

feathery plates melting at 134°, the isomeric *β-compound* melting at 36°, and the γ-compound at 101°. *a-Picoline methyl pentiodide*, C_6H_7N,MeI,I_4, forms bluish-black needles melting at 60°, the *β-compound* is a brown-black oil which does not solidify at −25°, and the γ-compound forms steel-blue needles melting at 63°. The *a-heptiodide* forms dark-green, feathery plates melting at 57°; and the *γ-heptiodide* dark-green, flat needles melting at 81·5°. *a-Picoline ethyl tri-iodide*, C_6H_7N,EtI,I_2, is a dark brown oil and the *pentiodide* a green-black oil. *Picoline propyl tri-iodide* and *pentiodide* are also oils. *Picoline isopropyl di-iodide*, $C_6H_7I,Pr^\beta I,I$, forms light brown cubes melting at 106°, and the *tri-iodide* long, silky, light-brown needles melting at 60°, whereas the *pentiodide* is a greenish-black oil. *Picoline butyl tri-iodide* forms flat, light-brown needles melting at 33°. *Picoline butyl pentiodide*, *picoline isobutyl tri-iodide*, the corresponding *pentiodide*, *picoline secondary butyl tri-iodide*, and *pentiodide* are all oils. *Picoline isoamyl di-iodide* melts at 96°, the *tri-iodide* at 22°, whereas the *pentiodide* is an oil. *Picoline allyl tri-iodide* crystallises in purple-brown needles melting at 62°, but the *pentiodide* is an oil.

Picoline hydrochloride, $C_6H_7N,HCl + \frac{1}{2}H_2O$, melts at about 200° and the anhydrous salt at about 80°; it is extremely deliquescent (compare Ramsay and also Anderson, *loc. cit.*). a-Picoline methyl chloride is also extremely hygroscopic and melts not very sharply at about 70°; the crystals contain $1H_2O$. *Picoline methobromide* forms long, colourless needles melting at 217°, *picoline ethobromide* melts at 97°, *picoline hydrogen dibromide*, C_6H_7N,HBr,Br, forms red rhombohedral crystals melting at 76°, the *tribromide* is a deep red oil. Ramsay (*loc. cit.*) describes a compound of the same composition melting at 85°. *a-Picoline methyl tribromide* crystallises in orange-yellow plates melting at 111°; *picoline ethyl tribromide* is a deep red oil. *Picoline hydriodide bromide*, C_6H_7N,HI,Br, obtained by mixing molecular proportions of picoline hydriodide and the hydriodide dibromide, forms dark-red crystals melting at 68°. *Picoline hydriodide dibromide* forms dark red crystals melting at 58°. *a-Picoline methiodide dibromide* is best obtained by mixing the tribromide (2 mols.) with the tri-iodide (1 mol.) and crystallising from alcohol; it forms slender, orange-red needles, two or three inches long, melting at 121·5°. *a-Picoline methiodide iodobromide*, C_6H_7N,MeI,IBr, crystallises in flat, interlaced needles of a reddish-brown colour melting at 113°. *Picoline allyliodide dibromide* crystallises in orange-yellow plates melting at 84°. The compounds described above are analogous to those of pyridine and with few exceptions agree with generalisations based on a study of the pyridine compounds (compare Prescott, *loc. cit.*). The normal iodides of picoline, as a rule, melt at a higher temperature than the corresponding pyridine iodides, and the same is more or less true of the periodides. In the case of complex perhaloids, the author thinks it probable that "it is the halogen of higher atomic weight that is next to the nitrogen" atom. J. J. S.

Action of Hydrogen Peroxide on Tertiary Bases. By Martin Auerbach and Richard Wolffenstein (*Ber.*, 1899, **32**, 2507—2520. Compare Abstr., 1898, i, 536).—*Propylpiperidine oxide*, $C_5H_{10}\cdot NPr^a\cdot O$,

obtained by allowing a mixture of propylpiperidine, acetone, and 5 per
cent. hydrogen peroxide to remain for 2 weeks, forms a hygroscopic,
crystalline mass, soluble in water, alcohol, or chloroform, but not in
ether or light petroleum.   Its halogen salts are extremely deli-
quescent, and the aurichloride is oily; the picrate is crystalline, and
melts at 105°.   In slightly acid solutions, it liberates iodine from
potassium iodide.   When heated with hydrochloric acid at 220° or
with nitrous acid at 100°, the oxide is reconverted into propyl-
piperidine; when heated, it evolves propylene, whilst δ-amidovaler-
aldehyde is left in the residue.

An additive product, 1-*oxy*-1-*propylpiperidinesulphonic anhydride*,

$C_5H_{10}NPr{<}{O \atop SO_2}$, is produced by passing sulphurous anhydride into a

solution of the oxide in water or chloroform; it melts at 131°, and is
soluble in chloroform, acetone, benzene, water, or ether; when
exposed to moisture, it is gradually converted into propylpiperidine
sulphate.

Isoamylpiperidine oxide is less hygroscopic than the preceding oxide,
and is prepared in a similar manner; its *hydrochloride* crystallises
with $1H_2O$; this is given off in the desiccator, and the dry salt melts at
102°; the hydriodide melts at 86°.   Isoamylpiperidine forms an *auri-
chloride* melting at 128° and a picrate melting at 133°; its oxide forms
an oily aurichloride and a *picrate* crystallising in needles and melting
at 112°, and does not react with platinic chloride.   Isoamylpiperidine
oxide is reconverted into isoamylpiperidine by heating it alone or with
hydrochloric or hydriodic acid; in the last case, the yield of tertiary
base is quantitative.   The *sulphonic anhydride* prepared by passing
sulphurous anhydride into an aqueous solution of the oxide, separates
in white crystals melting at 141°; in the presence of barium chloride,
isoamylpiperidine hydrochloride and barium sulphate are produced.
Benzylpiperidine oxide, $C_5H_{10}{:}N(CH_2Ph){:}O$, crystallises from acetone
and ether in lustrous, radiating needles containing $\frac{1}{2}H_2O$; the *picrate*
melts at 128°; the halogen salts are uncrystallisable, and the platini-
chloride is oily; the sulphonic anhydride melts at 131—132°.
Hydrogen peroxide has no oxidising action on the acidylpiperidines;
the presence of an acidic group seems to prevent the formation of a
derivative of pentavalent nitrogen.

Propionylpiperidine, prepared by heating piperidine with ethylic
propionate for 5 hours at 250°, is a liquid boiling at 230°, and very
soluble in ether or water.   *Isovalerylpiperidine* boils at 248° and is in-
soluble in water.   G. T. M.

Stereochemistry of the Piperidine Series. By W. HOHENEMSER
and RICHARD WOLFFENSTEIN (*Ber.*, 1899, 32, 2520—2524).—The re-
placement of the imidic hydrogen of an optically active piperidine
base by an alkyl radicle produces a marked increase in the specific
rotation; for 2-methylpiperidine $[\alpha]_D + 32°$, whilst for 2-methyl-1-
ethylpiperidine it is $+101 \cdot 06°$; on the other hand, the addition of the
alkyl group to the side chain attached to the asymmetric carbon atom
tends to diminish the optical activity, 2-propylpiperidine having a specific
rotation of $+15 \cdot 7°$. The dextrorotatory forms of 1-ethyl-, 1-propyl-, and

1-isoamyl-pipecoline were obtained from the inactive bases by means of d-tartaric acid ; their molecular rotations were + 128·3, 141·4, and 150·1 respectively. The melting points of the following salts of 1-isoamyl-a-pipecoline are given :

Picrate	inactive	105°	active	− 116°	active	+ 115°
Platinochloride	,,	130—135°	,,	187—188°	,,	181—182°
Hydrobromide	,,	deliquescent	,,	163°	,,	161° (indef.)
Hydrochloride	,,	,,	,,	155°	,,	150°
Mercurichloride	,,	oily	,,	oily	,,	oily.

1-*Isoamyl-2-pipecoline*, prepared by heating pipecoline with isoamylic bromide and solid potash for 16 hours at 125—130°, boils at 204—205° under 774 mm. pressure, and has a sp. gr. 0·8310 at 19°.   G. T. M.

Stereochemistry of the Piperidine Series. By ARTHUR MARCUSE and RICHARD WOLFFENSTEIN (*Ber.*, 1899, **32**, 2525—2531).—2 : 6-Di-methylpyridine (lutidine) was isolated from crude β-picoline by fractional distillation of the basic mixture and crystallisation of the picrate and hydrobromide ; the latter salt is far less deliquescent than was formerly stated, it is stable on exposure to the atmosphere, and melts at 210°. On reduction with sodium and ethylic alcohol, 2 : 6-di-methylpyridine yields 2 : 6-dimethylpiperidine (lupetidine), and a new isomeride, *isolupetidine* ; the two bases are separated by washing their hydrochlorides with acetone, when the isolupetidine salt passes into solution. The following salts of lupetidine were prepared : the *hydro-bromide*, melting at 285° ; the *acid tartrate*, melting at 79°, and the *picrate* at 162—164°. Lupetidine is inactive, and appears to be the meso-derivative, for it could not be separated into optically active forms by the tartrate method. Isolupetidine boils at 132—133° under standard pressure. The *hydrochloride* melts at 232—234°, the *hydro-bromide* at 245°, the *picrate* at 124—127·5°, and the *thiocarbamate* at 124—125°; the bitartrate has not been obtained in a crystallised form.
    G. T. M.

Action of Phosphorus Tribromide on Isomeric Monatomic Saturated Alcohols. Allylpiperidine. Allyldipropylamine. By NICOLAI A. MENSCHUTKIN (*Chem. Centr.*, 1899, i, 1066—1067 ; from *J. Russ. Chem. Soc.*, 1899, **31**, 43—45).—By the action of phosphorus tribromide on ethylic, isobutylic, isopropylic, and tertiary amylic alcohol, large yields of the corresponding monobromides are obtained in a pure state, and the residue from the distillation consists of almost pure phosphorous acid.

When a mixture of solutions of piperidine and allylic bromide in benzene is heated on the water-bath, a theoretical yield of almost pure piperidine hydrobromide (which does not contain any diallylpiperidine ammonium hydrobromide) is obtained, and the filtrate, when fraction-ated, yields *allylpiperidine*. The latter boils at 151—152° and has a sp. gr. 0·8445 at 18·5° ; the *aurichloride* forms a tough mass which is only soluble in hot water ; the *platinochloride*, $(C_3H_5 \cdot C_5NH_{10})_2, H_2PtCl_6$, crystallises in dark orange prisms.

By the action of dipropylamine on allylic bromide dissolved in benzene, an almost theoretical yield of dipropylamine hydrobromide is obtained, and the solution yields *allyldipropylamine*, which boils at 150—152° and has a sp. gr. 0·7587 at 16°. The hydrochloride deliquesces

on exposure to the air, and by adding auric chloride to the solution the *aurichloride*, $C_3H_5 \cdot NPr_2, HAuCl_4 + 2H_2O$, melting at 88—89°, is formed with separation of gold. The *platinochloride*, $(C_3H_5 \cdot NPr_2)_2, H_2PtCl_6 + H_2O$, forms clear, orange crystals.

The preparation of these allyl compounds is not complicated by bye-reactions as in the case of the action of methylic bromide on ammonia (compare Dübowsky, this vol., i, 854). E. W. W.

Nitroso-indoles. By ANGELO ANGELI and MATTEO SPICA (*Gazzetta*, 1899, **29**, i, 500—503).—When treated with nitrous acid, indoles with substituent alkyl radicles in the 3'- or 2':3'-positions, give true nitrosamines, whilst if the alkyl group be in the 2'-position only, compounds are obtained which have been regarded as nitroso-derivatives. Thus 2'-phenylindole yields a nitroso-2'-phenylindole, which is a yellow substance dissolving in alkali solutions with intense orange coloration, and readily yielding an acetyl derivative ; it does not react with hydroxylamine. These properties are not in accord with those of the true nitroso-derivatives, which are coloured green or blue, and react with hydroxylamine, giving, in the case of aromatic derivatives, diazo-compounds, and in the case of the nitrosamines, the primitive amine with evolution of nitric oxide. From these considerations, the authors are of opinion that nitroso-2'-phenylindole is represented by the formula $N{<}^{C_6H_4}_{CPh}{>}C{:}NOH$, corresponding with the ketone $N{<}^{C_6H_4}_{CPh}{>}CO$. This formula, containing the grouping
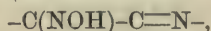
$$-C(NOH)-C{=}N-,$$

bears out the analogy which these compounds show to the nitroso-phenols which contain the chain $-C(NOH)-C{=}C-$. T. H. P.

3'-Nitroso-indoles. By MATTEO SPICA and F. ANGELICO (*Gazzetta*, 1899, **29**, ii, 49—60).—The authors regard 3'-nitroso-indoles as containing the group NOH united to the carbon atom in the 3'-position of the indole nucleus. Such a constitution would indicate a method of preparation of these compounds by acting on the indole with amylic nitrite in presence of sodium ethoxide, and this method is now shown to give almost quantitative yields of nitroso-indoles identical with those obtained by means of nitrous acid in acid solution.

Isonitroso-2'-phenylindole gives an *acetyl* derivative, $C_8H_4NPh{:}NOAc$, crystallising from light petroleum in shining, red needles melting at 121°, and a *benzoyl* derivative, which separates from benzene in brilliant red needles, soluble in alcohol, and slightly so in light petroleum, and melting at 151—152° without decomposing.

Isonitroso-2'-methylindole, $C_8H_4NMe{:}NOH$, obtained from 2'-methyl-ketole, separates from alcohol in brilliant, yellowish-green plates which change in the air and melt with decomposition at 198° ; acetic acid dissolves it, forming an intensely reddish-brown solution. It has both a basic and an acid character, yielding a potassium salt and a hydro-chloride ; with benzaldehyde, it gives no condensation product, showing that the indole character is lost. Its stability towards permanganate in alcoholic solution points to the absence of a double linking between

two carbon atoms. The *potassium* salt, $C_9H_7ON_2K$, forms orange-yellow, acicular crystals which, in the air, rapidly absorb moisture and carbonic anhydride and decompose.

Isonitroso-2'-methylindole hydrochloride forms an olive-green, crystalline mass which readily loses hydrogen chloride in the air, and is soluble in water with partial decomposition.

Isonitrosopyrroline, $C_4H_3N{:}NOH$, obtained by the action of amylic nitrite on pyrroline in presence of sodium ethoxide, is a yellowish-brown precipitate which rapidly blackens in the air. Its *sodium* derivative forms orange-coloured crystals. T. H. P.

Constitution and Reactions of "Isatoic Acid." By ERNST ERDMANN (*Ber.*, 1899, 32, 2159—2172).—Kolbe's isatoic acid (Abstr., 1885, 58) has, according to E. von Meyer, the constitution $C_6H_4{<}^{N \cdot COOH}_{CO}$, whereas Niementowski and Rozański (Abstr., 1889, 996) represent it by the formula $C_6H_4{<}^{NH \cdot CO}_{CO \cdot O}$. The author brings forward the following reasons for supporting the second constitution: 1. Methylic chlorocarbonate reacts with anthranilic acid in the same manner as the ethylic salt, yielding phenylurethanecarboxylic acid melting at 181°, and this is identical with the product formed by the action of methylic alcohol on "isatoic acid." 2. Phenylurethane-carboxylic acid, when etherified with methylic alcohol, yields a neutral etheric salt melting at 61°, which is also obtained when methylic chlorocarbonate reacts with methylic anthranilate. 3. "Isatoic acid" is most readily obtained by the action of carbonyl chloride on an aqueous solution of sodium anthranilate. "Isatoic acid" is thus not an acid, but the anhydride of a dicarboxylic acid, $COOH \cdot C_6H_4 \cdot NH \cdot COOH$. The author calls this dibasic acid isatoic acid, and the anhydride, previously known as isatoic acid he terms *isatoic anhydride*. The formation of the anhydride by the action of ethylic chlorocarbonate on anthranil at 140° is easy to understand if the old formula, $C_6H_4{<}^{NH}_{CO}{>}$, for anthranil is accepted and the formation of an additive product, $COCl \cdot C_6H_4 \cdot NH \cdot COOEt$, assumed, as this, by loss of ethylic chloride, would give isatoic anhydride.

A yield of some 50 per cent. of the anhydride is obtained by Niementowski and Rozański's method, provided an excess of ethylic chlorocarbonate is employed and the mixture is boiled long enough. The simplest method is, however, to pass carbonyl chloride into an aqueous solution of sodium anthranilate, and to crystallise the precipitated anhydride from alcohol; it is thus obtained in the form of glistening prisms; it crystallises from its aqueous solutions in colourless needles; the temperature at which it decomposes appears to vary greatly (240—290°), according to the medium from which it crystallises. The anhydride has no acid reaction towards moist litmus paper, and dissolves but slowly in cold sodium carbonate solution, and may be precipitated unchanged on the addition of acids. Prolonged contact, however, with sodium carbonate decomposes it into carbonic anhydride and anthranilic acid, together with an acid, $C_{15}H_{12}O_6N_2$, probably

diphenylcarbamidedicarboxylic acid, $CO(NH \cdot C_6H_4 \cdot COOH)_2$. A better yield of this acid is obtained when hot sodium carbonate solution is employed; it crystallises from dilute alcohol, melts and decomposes at 165°, has a strongly acid reaction, is readily soluble in alcohol, and only very sparingly in water; when heated with lime, it yields diphenylamine and aniline. Its *sodium* salt, $C_{15}H_{10}O_5N_2Na_2 + H_2O$, forms colourless, crystalline crusts, and is readily soluble in water.

When isatoic anhydride is heated with methylic alcohol at 130° (compare Schmidt and Meyer, Abstr., 1888, 371), the chief product is *methylic hydrogen isatoate* (phenylurethanecarboxylate), $COOH \cdot C_6H_4 \cdot NH \cdot COOMe$, which crystallises from dilute alcohol in colourless needles melting at 181°; it is identical with the product formed by the action of methylic chlorocarbonate on anthranilic acid, and also with the compound described by Schmidt as methylic carboxyanthranilate. In addition to the acid etheric salt described above, an oily bye-product containing anthranilic acid, methylic anthranilate, and dimethylic isatoate is also formed. It has been found impossible to convert the acid etheric salt into methylic anthranilate, either by heating with methylic alcohol or with glycerol (compare Schmidt, *loc. cit.*); with the latter reagent, a small quantity of a volatile syrupy base has been obtained, but its constitution has not been determined.

Dimethylic isatoate, $COOMe \cdot C_6H_4 \cdot NH \cdot COOMe$, is best obtained by boiling equal quantities of methylic chlorocarbonate and methylic anthranilate for an hour; it may also be obtained by further etherifying the acid etheric salt; it crystallises in glistening, white needles melting at 61°, is readily soluble in alcohol, but only sparingly in benzene, and is readily volatile in steam.   **J. J. S.**

Formation of 2'-Alkylquinoline-4'-carboxylic Acid. By KARL GARZAROLLI-THURNLACKH (*Ber.*, 1899, **32**, 2274—2277).—Doebner (Abstr., 1887, 504; 1888, 300) first prepared 2'-phenylquinoline-4'-carboxylic acid by the interaction of aniline, benzaldehyde, and pyruvic acid in benzene solution at 100°; at the same time, a neutral substance, $C_{22}H_{18}ON_2$, was also formed, which had previously been obtained by him from the same condensation in ethereal solution at the ordinary temperature.

The author considered that in this reaction either (I) the benzylideneaniline formed by the condensation of benzaldehyde with aniline combined with pyruvic acid to form α-keto-γ-anilidophenylbutyric acid, $NHPh \cdot CHPh \cdot CH_2 \cdot CO \cdot COOH$, or (II) the benzylideneaniline combined with pyruvic acid to form $NPh\overset{..}{:}CMe \cdot COOH$ and benzaldehyde, which again condensed to form α-anil-γ-hydroxyphenylbutyric acid,

$$OH \cdot CHPh \cdot CH_2 \cdot C(NPh) \cdot COOH.$$

In the first case, by the elimination of water, 2'-phenyldihydroquinoline-4'-carboxylic acid would be produced, which by the elimination of 2 atoms of hydrogen and rearrangement would be transformed into 2'-phenylquinoline-4'-carboxylic acid; in the second case, by a similar process, 4'-phenylquinoline-2'-carboxylic acid would be formed.

In order to settle this point, molecular quantities of benzylideneaniline and pyruvic acid were warmed togther in alcoholic solution, when Doebner's neutral substance, $C_{22}H_{18}ON_2$, separated, and from the

mother liquors 2'-phenylquinoline-4'-carboxylic acid was obtained, and showed complete identity with Doebner's acid.

It is evident that Doebner and von Miller's quinaldine synthesis can be explained in the same way. **J. F. T.**

5-Chloro-1-phenyl-3-methylpyrazole. By August Michaelis and R. Pasternack (*Ber.*, 1899, **32**, 2398—2412).—This oily substance, obtained by heating 1-phenyl-3 : 4-dimethyl-5-pyrazolone with phosphorus oxychloride (this vol., i, 233), is not a chlorophenyldimethylpyrazole, as was at first supposed, but 5-*chloro*-1-*phenyl*-3-*methylpyrazole*,

$$NPh\left\langle\begin{array}{l}N=CMe\\CCl{:}CH\end{array}\right.$$ It is formed by the elimination of methylic chloride

from the methochloride of chlorophenylmethylpyrazole produced in the first stage of the reaction. It is most easily obtained by heating 1-phenyl-3-methyl-5-pyrazole with phosphorus oxychloride, and forms a thick, colourless liquid with a characteristic odour, and boils unaltered at 261° under ordinary pressures, at 148° under 20 mm., and at 134° under 10 mm. pressure ; it has a sp. gr. 1·1999 at 18°. It is a feeble base and dissolves in fairly concentrated sulphuric acid, but is reprecipitated by much water. The *hydrochloride*, $C_{10}H_9N_2Cl,HCl$, produced by leading hydrogen chloride into an ethereal solution of the base, is very hygroscopic, decomposes on exposure to the air, and melts at 87—88°. The *platinochloride*, $(C_{10}H_9N_2Cl)_2,H_2PtCl_6 + 2H_2O$, forms broad leaflets, loses water at 100°, and melts at 174°.

5-*Chloro*-1-*phenyl*-3-*methylpyrazole methochloride*, $NPh\left\langle\begin{array}{l}NMeCl{:}CMe\\CCl{-}{-}{-}CH\end{array}\right.$,

is formed when antipyrine is heated with phosphorus oxychloride at 150° ; it forms large, transparent crystals containing $1H_2O$, which become moist on exposure to the air, and effloresce on exposure in a vacuum over sulphuric acid ; it dissolves readily in water, alcohol, or chloroform, but is insoluble in ether ; the hydrated crystals fuse at 116—117°, but the anhydrous substance melts at 224°, and at higher temperatures breaks up into methylic chloride and chlorophenylmethylpyrazole. The aqueous solution gives precipitates with phosphotungstic and phosphomolybdic acids, potassium mercuric iodide, potassium, cadmium, or bismuth iodide, platinic and auric chlorides, and with bromine water. The *platinochloride*, $(C_{10}H_9N_2MeCl)_2PtCl_6$, crystallises from hot water in yellowish-brown leaflets melting at 218°. The *aurichloride*, $(C_{10}H_9N_2MeCl)_2AuCl_4$, forms light yellow leaflets and melts at 145°. The *mercurichloride*, $C_{10}H_9N_2Cl,MeCl,HgCl_2$, forms compact, transparent crystals which melt indefinitely at 98°.

By heating the methochloride with a 10 per cent. solution of sodium hydroxide, antipyrine is formed.

The *methobromide*, $NPh\left\langle\begin{array}{l}NMeBr{:}CMe\\CCl{=}{=}CH\end{array}\right.$, crystallises from a mixture

of absolute alcohol and ether in long, white needles, and melts at 256°. A *perbromide*, $C_{11}H_{12}N_2ClBr_3$, is obtained on adding bromine to a solution of the methochloride in glacial acetic acid ; it crystallises from hot alcohol in yellow leaflets and melts at 136°, and when boiled with water yields the foregoing methobromide.

The *methiodide*, $NPh{<}^{NMeI:CMe}_{\;CCl=CH}$, forms long, colourless needles, is sparingly soluble in cold water, but dissolves readily in hot water, and is insoluble in ether. A *periodide*, $C_{11}H_{12}N_2ClI,I_4$, is formed when a solution of iodine in potassium iodide is added to an aqueous solution of the methochloride; it crystallises from hot water in dark, iodine-like leaflets having a green surface colour, dissolves very sparingly in water, but is readily soluble in hot alcohol and glacial acetic acid, and readily parts with iodine.

5-Iodo-1-phenyl-3-methylpyrazole ethiodide, $NPh{<}^{NEtI:CMe}_{\;Cl=CH}$, produced when the chloropyrazole is heated with excess of ethylic iodide for 6 hours at 100°, forms long, white needles, is nearly insoluble in cold water, but dissolves readily in boiling water and hot alcohol, and melts and decomposes at 240°. When it is heated with moist silver chloride, the *ethochloride*, $C_{10}H_9N_2I,EtCl$, is formed; this melts and decomposes at 222°, yielding ethylic chloride and 5-iodo-1-phenyl-3-methylpyrazole as a brownish liquid.

When chlorophenylmethylpyrazole, dissolved in light petroleum, is warmed with excess of bromine, a *perbromide*, $C_{10}H_8N_2ClBr_3$, is obtained. This forms a yellow, unstable powder which cannot be purified by recrystallisation, and readily loses 2 atoms of bromine. It dissolves in hot alcohol, decomposing slightly, and melts at 99°. When it is heated with sodium hydroxide until all colour is removed, it yields *5-chloro-4-bromo-1-phenyl-3-methylpyrazole*, $NPh{<}^{N=CMe}_{CCl:CBr}$, a substance which crystallises in slender, silky, white needles, is soluble in strong hydrochloric acid, and melts at 56°.

4 : 5-Dichloro-1-phenyl-3-methylpyrazole, $NPh{<}^{N=CMe}_{CCl:CCl}$, may be prepared by the direct chlorination of the corresponding monochloro-compound with chlorine or phosphorus pentachloride; it crystallises from alcohol in white needles, and melts at 155°. When heated at 100—120° with methylic iodide, it yields *5-chloro-1-phenyl-3-methyl-4-iodopyrazole methiodide*, $NPh{<}^{NMeI:CMe}_{\;CMe=CI}$, which separates from hot water in long, white needles, and melts and decomposes at 229°.

4 : 5-Dichloro-1-parachlorophenyl-3-methylpyrazole,

$$C_6H_4Cl\cdot N{<}^{N=CMe}_{CCl:CCl}$$
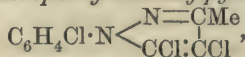
is formed when chlorine is passed into the monochloropyrazole for a long time; it crystallises from hot alcohol in white needles melting at 130°, is sparingly soluble in cold alcohol, but readily in the hot liquid, and dissolves in strong hydrochloric acid.

5-Chloro-1-phenyl-3-methylpyrazole-4-phosphinic acid,

$$NPh{<}^{N=CMe}_{CCl:C\cdot PO(OH)_2}$$
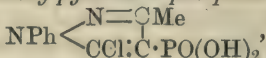
is formed in small quantity when phosphorus oxychloride acts on antipyrine and the product is treated with water; it may also be ob-

tained in a similar manner from chlorophenylmethylpyrazole or its methochloride; it separates from hot water in compact, white leaflets which melt at 191°, is sparingly soluble in ether or cold water, but is somewhat readily dissolved by hot water or alcohol. The *silver* salt, $C_{10}H_8N_2Cl \cdot PO(OAg)_2$, is a white, amorphous powder insoluble in water, but readily dissolved by aqueous ammonia. The phosphinic acid is completely decomposed, when heated alone or with strong hydrochloric acid at 150°, into metaphosphoric acid and chlorophenyl-methylpyrazole.   A. L.

Some Amido-α-phenylbenzimidazole Derivatives. By OTTO KYM (*Ber.*, 1899, **32**, 2178—2180. Compare this vol., i, 647, for analogous benzoxazoles).—Benzodinitranilide and 2'-phenyl-2-amido-benzimidazole (Muttelet, this vol., i, 500) can be obtained, the first by heating 1 : 2 : 4-dinitraniline with benzoic chloride at 160—180°, the second by reducing this first product with stannous chloride and hydrochloric acid; the *acetyl* derivative of the second substance melts at 245—246° when dry. The pale yellow *paranitrobenzodinitranilide*, $C_6H_3(NO_2)_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot NO_2$, melting at 195—196°, can be obtained in a similar manner, and reduced to *paramido-2'-phenyl-2-amidobenz-imidazole*, $NH_2 \cdot C_6H_3 <^{NH}_{N}>C \cdot C_6H_4 \cdot NH_2$; this melts at 235—236° when dry; its *acetyl* derivative melts above 305°.   C. F. B.

Oxidation of Alkylhalides of Benzimidazoles. By JOHANNES PINNOW and CARL SÄMANN (*Ber.*, 1899, **32**, 2181—2191).—*2 : 1' : 2'-Trimethylbenzimidazole methochloride*, $C_6H_3Me <^{NMe}_{NMeCl}>CMe$, is obtained from the corresponding methiodide (Niementowski, Abstr., 1887, 937) by treating this with lead acetate and hydrochloric acid in succession. Potassium permanganate oxidises it at 90—95° to *phenylenedimethylcarbamide-carboxylic* (1' : 3'-*dimethylbenzimidazolone*-2-*carboxylic*) *acid*, $COOH \cdot C_6H_3 <^{NMe}_{NMe}>CO$; this melts at 281—282°; its *calcium* and *lead* salts crystallise each with $3H_2O$; when nitrated, it yields a *dinitrophenylenedimethylcarbamide*, $C_6H_2(NO_2)_2 <^{NMe}_{NMe}>CO$, which remains unmelted at 270°. In the oxidation mentioned above, some *tolylenedimethylcarbamide* (2 : 1' : 3'-*trimethylbenzimidazolone*), $C_6H_3Me <^{NMe}_{NMe}>CO$, is formed also. The carboxylic acid described is also formed when the methochloride of 2 : 1'-dimethylbenzimidazole (Abstr., 1898, i, 182) is oxidised with permanganate at 55—100°; this *methochloride* melts at 228—229°, and crystallises with $1H_2O$; the *methiodide* was analysed also. Trimethylbenzimidazole *ethobromide*, which is formed much less readily than the methiodide and melts at 236—237°, behaves like its methyl analogue when oxidised with permanganate at 48—65°, but gives a far worse yield; 1'-*methyl-3'-ethyl-benzimidazolone-_-carboxylic acid* melts at 233—234°.

1' : 2-Dimethylbenzimidazole (phenylenemethylethenylamidine) *metho-chloride*, $C_6H_4 <^{NMe}_{NMeCl}>CMe$, is obtained from the corresponding

methiodide (O. Fischer, Abstr., 1892, 1475); it melts at 225—230°, and crystallises with $2H_2O$; when oxidised with permanganate at the ordinary temperature, at 47—52°, and at 57—64° in succession, it yields *phenylenedimethylcarbamide*, $C_6H_4 <^{NMe}_{NMe}> CO$, which melts at 108·5—110°. This substance is also formed when the sodium salt of phenylenemethylcarbamide is heated at 103—106° with methylic iodide in methyl alcoholic solution. *Phenylenemethylcarbamide*, $C_6H_4 <^{NMe}_{NH}> CO$, is obtained by heating orthonitraniline hydrobromide with methylic alcohol at 100°, reducing the methylnitraniline formed to amidomethylaniline, and condensing this with carbonyl chloride in benzene-toluene solution; it melts at 191—192°. 1′ : 2′-Dimethylbenzimidazole methochloride is converted by sodium methoxide, or by caustic potash on heating, into 1′ : 2′ : 3′-*trimethylbenzimidazolinol*, $C_6H_4 <^{NMe}_{NMe}> CMe·OH$; this melts at 164—165°.

C. F. B.

Orthamidophenetidine. By GEORG COHN (*Ber.*, 1899, **32**, 2239—2243).—The following experiments were undertaken with the object of ascertaining the effect of various constitutional changes on the physiological effect of a compound. 3-*Ethoxybenzimidazolone*, $OEt·C_6H_3 <^{NH}_{NH}> CO$, is prepared by the action of phosgene on orthamidophenetidine, and crystallises in lustrous, white plates melting at 266—268°. The compound has not a sweet taste, although it is closely related in constitution to dulcine, $OEt·C_6H_4·NH·CO·NH_2$.

3-*Ethoxyphenylene-ethenyldiamine*, 3-ethoxy-2′-methylbenzimidazole, $OEt·C_6H_3 <^{NH}_{N}> CMe$, is best obtained by the action of acetic anhydride and sodium acetate on amidophenetidine, and forms a white, crystalline powder melting at 149—150°. The *hydrochloride* is a white, soluble powder which has a bitter taste. This compound is not an anæsthetic, although the compound

$$OEt·C_6H_4·NH·CMe\!:\!N·C_6H_4·OEt,$$

with which it is closely related, has anæsthetic properties.

Ethoxymethylbenzimidazole is accompanied by *diacetylamidophenetidine*, which melts at 188°, and by a blue colouring matter. Methylic iodide converts it into 3-*ethoxy*-1′ : 2′-*dimethylbenzimidazole hydriodide*, $OEt·C_6H_3 <^{NMe}_{N}> CMe,HI$, which crystallises in fascicular groups of long needles; the *base* forms slender needles melting at 102°. 3-*Ethoxy*-2′-*isobutyrylbenzimidazole*, $CHMe_2·CO·C <^{NH}_{N}> C_6H_3·OEt$, obtained by the action of isovaleric acid on the benzimidazole, melts at 135—136°.

A. H.

Preparation of 3′-Phenyldihydroquinazoline (Orexine). By VICTOR KULISCH (*Chem. Centr.*, 1899, i, 847; from *Zeit. Österr. Apoth.-V.*, **37**, 138—141).—Quinazoline and its homologues containing alkyl groups in the miazine ring may be prepared by the condensation of
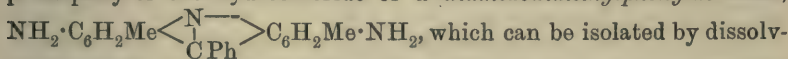
orthamidobenzaldehyde with formamide, or an amide of a higher acid. By heating orthamidobenzoic acid (1 mol.) with formanilide (1 mol.) at 123—130° for an hour, a compound is obtained which is identical with Paal and Busch's 3′-phenyl-4-ketoquinazoline,

$$C_6H_4 \!\! \begin{array}{c} \diagup N \!\! = \!\! CH \\ \diagdown CO \cdot NPh \end{array},$$
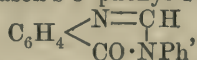
prepared by oxidising orexine with potassium permanganate (Abstr., 1890, 72). This compound crystallises from ether in slightly yellow, rhombic crystals, and when reduced in alkaline solution with tin and hydrochloric acid, yields the dihydro-compound, orexine, $C_{14}H_{12}N_2$, which crystallises in small, lustrous plates and melts at 94—96°.

E. W. W.

Benzoflavines. By RICHARD E. MEYER and RUDOLF GROSS (*Ber.*, 1899, **32**, 2352—2371).—Oehler's "Benzoflavine, 6B.F.O.," consists principally of the hydrochloride of a *diamidodimethylphenylacridine*,

$$NH_2 \cdot C_6H_2Me \!\! \begin{array}{c} \diagup N \!\! - \!\! - \!\! \diagdown \\ \diagdown CPh \diagup \end{array} \!\! C_6H_2Me \cdot NH_2,$$ which can be isolated by dissolv-

ing the dye in dilute acetic acid and precipitating with caustic soda; the base crystallises from alcohol in brownish-yellow, stunted prisms, and yields a *hydrochloride*, $C_{21}H_{19}N_3, 2HCl + H_2O$, crystallising in brownish-red needles, a *hydriodide*, $C_{21}H_{19}N_3, HI$, which forms brownish-yellow, elongated plates, a *hydrobromide*, $C_{21}H_{19}N_3, HBr$, crystallising from alcohol in rhombic pyramids and from acetic acid in long, brownish-red needles, and a *sulphate*, which separates in long, red prisms; all these salts dissolve in alcohol with a green fluorescence.

When benzaldehyde is added to an alcoholic solution of equivalent quantities of $1:2:4$-tolylenediamine and its hydrochloride at 60°, *tetramidoditolylphenylmethane hydrochloride*, $C_{21}H_{24}N_4, 4HCl + 2H_2O$, is precipitated in the form of bright yellow plates; the *base*, $CHPh[C_6H_2Me(NH_2)_2]_2$, crystallises from chloroform in beautiful, rhombic plates and melts at 230—231°. *Benzylidenemetatolylenediamine*, $CHPh\!:\!N \cdot C_6H_3Me \cdot NH_2$, the intermediate product of this action, can be prepared by adding benzaldehyde to $1:2:4$-tolylenediamine suspended in water; it forms large, yellow plates, melts at 90—91°, is easily hydrolysed by dilute acids at the ordinary temperature, and, when warmed with metatolylenediamine hydrochloride in alcoholic solution for 3 hours at 60—70°, is converted into tetramidoditolylphenylmethane hydrochloride. When the latter is heated with dilute hydrochloric acid of sp. gr. 1·07 for 7 hours at 160°, ammonia is eliminated, and a mass of red needles of the hydrochloride of *diamidodihydrophenylacridine*, $CHPh\!\! \begin{array}{c} \diagup C_6H_3(NH_2) \\ \diagdown C_6H_3(NH_2) \end{array} \!\! NH$, formed;

this, however, cannot be isolated, owing to the ease with which it is oxidised by the air, to form the benzoflavine hydrochloride described above; the formation of the latter is accelerated by adding ferric chloride.

Attempts to diazotise "benzoflavine, 6B.F.O.," by the usual methods, using sodium or amylic nitrite, failed, but by passing nitrous acid fumes into a solution of the base in concentrated sulphuric acid and subsequently adding the diazo-solution obtained to boiling alcohol,

the two amido-groups were eliminated, and *μ-phenyl-2 : 7-dimethyl-acridine*, $\begin{array}{c}\mathrm{CH{:}CH-C{\cdot}N{\longrightarrow}C{\cdot}CH{:}CH}\\ \mathrm{CMe{:}CH{\cdot}C{\cdot}C Ph{\cdot}C{\cdot}CH{:}CMe'}\end{array}$, formed ; this crystallises from alcohol, chloroform, or benzene in needles, from light petroleum in light yellow, rhombic plates, melts at 166—167°, and dissolves in acids with a green fluorescence. The *hydrochloride*, $C_{21}H_{17}N,HCl$, and the *hydrobromide* form bright yellow plates, the *hydriodide* crystallises in fan-shaped aggregates, the *sulphate*, $C_{21}H_{17}N,H_2SO_4$, in prisms, and the *methiodide*, $C_{21}H_{17}N,MeI$, in long, red needles which melt at 186—187°. The structure of the base follows from its being formed on heating paraditolylamine with benzoic acid and zinc chloride for 10 hours at 260° ; from this, taking into account recent views as to the structure of fluorescein, the authors attribute to " *benzoflavine, 6B.F.O.*," the constitution $\begin{array}{c}\mathrm{NH_2{\cdot}C{:}CH{\cdot}C{\cdot}N{\longrightarrow}C{\cdot}CH{:}C{\cdot}NH_2}\\ \mathrm{MeC{:}CH{\cdot}C{\cdot}C Ph{\cdot}C{\cdot}CH{:}CMe}\end{array}$, although two other formulæ are possible.

An attempt to decide between these by eliminating the carboxyl group of the compound $C_{20}H_{15}O_2N_3$, obtained by the action of ammonia on fluorescein (Meyer and Oppelt, Abstr., 1891, 246), which has since been shown to be a diamidophenylacridinecarboxylic acid, $\begin{array}{c}\mathrm{NH_2{\cdot}C{:} CH{\cdot} C{\cdot}N{\longrightarrow}C{\cdot}CH{:}C{\cdot}NH_2}\\ \mathrm{CH{:}CH{\cdot}C{\cdot}C(C_6H_4{\cdot}COOH){\cdot}C{\cdot}CH{:}CH}\end{array}$ (German Patents, 1893, 73334 and 75933), led to no issue ; moreover, the *diamidophenylacridine*, $\begin{array}{c}\mathrm{NH_2{\cdot}C{:} CH{\cdot} C{\cdot}N{\longrightarrow}C{\cdot}CH{:}C{\cdot}NH_2}\\ \mathrm{CH{:}CH{\cdot}C{\cdot}C Ph{\cdot}C{\cdot}CH{:}CH}\end{array}$, which should have been the product of this action, could not be obtained in a pure state by the interaction of benzaldehyde with metaphenylenediamine. The interaction of these substances in molecular proportion yields *dibenzylidenemetaphenylenediamine*, $C_6H_4(N{:}CHPh)_2$, which crystallises from ether in aggregates of yellow needles and melts at 104—105°.

The authors confirm the statements contained in the German patents cited above with reference to the fluorescein derivative, $C_{20}H_{15}O_2N_3$; the *ethylic salt*, $C_{20}H_{14}O_2N_3Et$, prepared according to these patents, crystallises from 50 per cent. alcohol in needles or plates, melts at 247—248°, and forms a crystalline *hydrochloride*, $C_{20}H_{14}O_2N_3Et,2HCl$.   W. A. D.

Oxy-compounds of Pyrrodiazole. By AMERIGO ANDREOCCI and V. MANNINO (*Gazzetta*, 1899, **29**, ii, 41—48. Compare Abstr., 1898, i, 277).—By means of phosphorus pentachloride, derivatives of urazole and of 3- and 5-pyrrodiazolone are reduced to pyrrodiazole compounds, and pyrazolones similarly yield pyrazoles. In the case of phenylurazole and paratolylurazole, however, Pellizzari and Ferro (this vol., i, 550) have shown that by moderating the action of the phosphorus pentasulphide, intermediate compounds consisting of phenyl- and tolylderivatives of 3-thiotriazolone and of 3-thiobistriazole are obtained. With a view to discovering the mechanism of the reducing action of the pentasulphide, the authors have attempted to reduce these thiocompounds to pyrrodiazole derivatives by means of hydrogen sulphide or ammonium sulphide, but negative results were obtained.
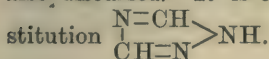
That the reducing action is not due to hydrogen phosphides is shown by the failure of the reaction of these phosphides with 1-phenyl-3-methyl-5-pyrrodiazolone to yield a reduction product; with the same compound, neither phosphorous acid nor ordinary phosphorus gave a definite product.

The action of phosphorus oxychloride on phenylpyrrodiazolone gives rise only to the formation of phosphorus compounds, but if the trichloride be present, phenylpyrrodiazole is obtained.

It is concluded that in the reduction of pyrrodiazolones by chlorine or sulphur compounds of phosphorus, the reducing action is not exerted directly on the pyrrodiazolone, but on intermediate chloro- or thio-derivatives. T. H. P.

Relation of 2 : 4-Pyrrodiazole to Benzene and to Cyclic Compounds of the Pyridine and Pyrroline Types. By AMERIGO ANDREOCCI (*Gazzetta*, 1899, **29**, ii, 1—22).—A detailed account is given of the synthetical processes which give rise to 2 : 4-pyrrodiazole and its derivatives, the general behaviour of the pyrrodiazole group and its analogies to benzene, pyrroline, 2-pyrrazole, and pyridine being also discussed. It is concluded that 2 : 4-pyrrodiazole has the constitution $\begin{smallmatrix} N=CH \\ | \\ CH=N \end{smallmatrix}\!\!>\!NH$. T. H. P.

Condensation of Diazomethane with Quinones. By HANS VON PECHMANN and EUGEN SEEL (*Ber.*, 1899, **32**, 2292—2300).—The first product of the action of diazomethane on quinone in ethereal solution is a white, unstable diazo-compound which soon becomes yellow, and when drained becomes brownish-red on exposure to air and generally explodes as soon as it is dry. If allowed to remain under the ether for one or two days, or, better, if mixed with one-third the volume of alcohol, cooled to 0° for one hour and extracted with dilute caustic soda, the diazo-compound passes into a stable iso-meride, *diketobenzobisdihydropyrazole*, $N\!\!<\!\!\begin{smallmatrix} CH \cdot CH \cdot CO \cdot CH \cdot CH \\ NH \cdot CH \cdot CO \cdot CH \cdot NH \end{smallmatrix}\!\!>\!N$ or $N\!\!<\!\!\begin{smallmatrix} CH \cdot CH \cdot CO \cdot CH \cdot NH \\ NH \cdot CH \cdot CO \cdot CH \cdot CH \end{smallmatrix}\!\!>\!N$, which separates on acidifying the alkaline solution with dilute sulphuric acid. It is a colourless powder, which begins to blacken at 280° and decomposes at 300°; is insoluble in the ordinary solvents, dissolves in caustic soda to a yellow solution from which strong alkali precipitates the yellow *sodium* derivative, and dissolves in sodium carbonate solution on boiling. It is not acted on by oxidising or reducing agents, but the insoluble *silver* derivative is acted on by methylic iodide and gives a product insoluble in alkalis. The *diacetyl* compound crystallises from a mixture of acetic acid and acetic anhydride in colourless or feebly-yellowish needles, becomes brown above 300°, does not dissolve in the ordinary solvents, but is at once hydrolysed by dilute alkalis. The *diphenylhydrazone* melts at 266°, crystallises from a mixture of acetone and benzene as a yellow, microcrystalline powder, is only slightly soluble in most solvents, but gives a blue solution in concentrated sulphuric acid, whilst the solution

in acetic acid gives a red coloration and then a reddish-brown precipitate with ferric chloride.

Diketonaphthadihydropyrazole, $N{<}{CH \cdot CH \cdot CO \atop NH \cdot CH \cdot CO}{>}C_6H_4$, prepared by the action of diazomethane on α-naphthaquinone, crystallises from glacial acetic acid in colourless needles, sublimes on heating, chars at 280°, dissolves only very slightly in ordinary solvents, but more readily in pyridine, dissolves in caustic alkalis to a greenish-yellow solution, and in sodium carbonate solution on boiling. The silver derivative, when treated with methylic iodide, gives a methylic derivative insoluble in alkalis; oxidising and reducing agents are without action on it ; bromine in chlorofom solution gives a red, crystalline *additive product* which loses its bromine on exposure to air. The *monobenzoyl* derivative crystallises from much alcohol in felted needles, melts at 185°, and dissolves readily in chloroform. The *monophenylhydrazone* crystallises from acetic acid in felted, brick-red needles, melts with decomposition at 272°, is sparingly soluble in most solvents, but dissolves in concentrated sulphuric acid to a violet solution, and in alcoholic potash to a green solution which becomes brown on adding water. The *monoxime* melts at 276°, crystallises from acetic acid or pyridine in needles, and dissolves in caustic alkalis to a yellow solution.

Dihydroxydiketonaphthadihydropyrazole,

$$N{<}{CH \cdot CH \cdot CO \atop NH \cdot CH \cdot CO}{>}C_6H_2(OH)_2,$$
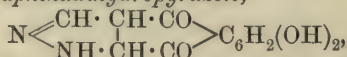
prepared by hydrolysis of the acetyl compounds, forms slender, orange-red needles, melts at 300°, is slightly soluble in the ordinary solvents, giving solutions which show a yellowish-green fluorescence ; it dissolves in concentrated sulphuric acid to a red solution with brownish-yellow fluorescence, and in alkalis to a magenta-red solution. The *diacetyl* derivative, prepared by the action of diazomethane on diacetylnaphthazarine, melts at 175°, crystallises from acetone in needles, is only slightly soluble in most solvents, more readily in pyridine or boiling acetic acid, and dissolves in alkalis to a violet solution, from which acids liberate the dihydroxy-compound as a red, flocculent precipitate. The *triacetyl* derivative crystallises from glacial acetic acid in greenish flakes, melts at 173° to an orange-coloured fluid, dissolves only very slightly in ordinary solvents, most readily in pyridine, gives a magenta-red solution in concentrated sulphuric acid, and is readily hydrolysed by acids or alkalis.

*Pyrazole*-4 : 5-*dicarboxylic acid*, $N{<}{CH \cdot C \cdot COOH \atop NH \cdot C \cdot COOH}$, prepared by oxidising the above triacetate with nitric acid, crystallises in white, glistening, efflorescent needles, with $1H_2O$, melts at 260° with evolution of gas, and dissolves readily in alcohol or water ; its constitution is shown by its preparation from methylic 4 : 5-pyrazolinedicarboxylate (Pechmann, Abstr., 1894, i, 438) by oxidation with nitric acid. The *methylic* salt, prepared by oxidising methylic 4 : 5-pyrazolinedicarboxylate with bromine, crystallises from hot water in white, felted needles, dissolves in most solvents, and melts at 141°,

On heating above the melting point, pyrazole-4 : 5-dicarboxylic acid loses carbonic anhydride and yields pyrazole. T. M. L.

Diazole Group. III. Phenyldithiodiazolonethiol. By MAX BUSCH and W. STRAMER (*J. pr. Chem.*, 1899, [ii], 60, 187—191. Compare this vol., i, 825).—The *ethylic ether* of phenyldithiodiazolonethiol, $NPh{<}^{N=C\cdot SEt}_{CS\cdot S}$, prepared by the action of ethylic iodide on the potassium derivative, crystallises from alcohol in large, silvery flakes, and melts at 66°. It forms an *iodine additive product*, $C_{10}H_{10}N_2I_2S_3$, which dissolves readily in hot benzene, and crystallises, on cooling, in splendid, dark-red prisms, melts at 123°, and is decomposed by bisulphite solution. The corresponding *bromide* melts at 131°, crystallises from benzene in magnificent orange-red, silky needles, and does not dissolve in cold alcohol, but is decomposed by it on heating. The *ethylenic ether*,

$$C_2H_4(S\cdot C_8H_5N_2S_2)_2,$$
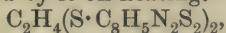
forms stout, transparent crystals, melts at 145°, dissolves readily in boiling benzene or chloroform, and slightly in alcohol, ether, or ethylic acetate. The *benzylic ether*, $C_8H_5N_2S_2\cdot S\cdot CH_2Ph$, separates from alcohol in stout, yellowish crystals, and melts at 93°. The *benzoyl* derivative, $C_8H_5N_2S_2\cdot SBz$, melts at 154°, crystallises from a mixture of chloroform and alcohol in glistening, white needles, and dissolves readily in boiling benzene or chloroform, but only slightly in other solvents.

When reduced with sodium amalgam, the thiol yields phenylthiodiazolinethiol, $NPh{<}^{N=C\cdot SH}_{CH_2\cdot S}$ (Abstr., 1896, i, 190). Diazobenzene chloride interacts with the potassium salt of the thiol to form the *diazosulphide*, $C_8H_5N_2S_2\cdot S\cdot N_2Ph$, an unstable, yellow precipitate readily soluble in ether, benzene, or alcohol.

Phenyldithiodiazolone bisulphide, when acted on with alcoholic potash, re-forms the thiol, but the sulphinic acid, $NPh{<}^{N=C\cdot SO_2H}_{CS\cdot S}$, which should also be produced, appears to be hydrolysed to phenyldithiodiazolone, $NPh{<}^{N=CH}_{CS\cdot S}$, and then to phenylthiourethane,

$$NHPh\cdot CS\cdot OEt,$$

which forms the chief product of the action. T. M. L.

Diazole Group. IV. Action of Amines on Phenyldithiodiazolone Bisulphide. By MAX BUSCH and JAS. WOLFF (*J. pr. Chem.*, 1899, [ii], 60, 192—196. Compare Abstr., 1896, i, 705).—The chief products of the action of orthophenylenediamine on phenyldithiodiazolone bisulphide are the *orthophenylenediamine* salt of phenyldithiodiazolonethiol, which forms long, rose-coloured needles, and melts at 180°, an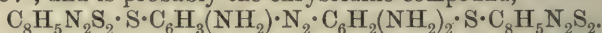d *phenyldithiodiazolonethiol orthodiamidophenylic ether*, $NPh{<}^{N=C\cdot S\cdot C_6H_3(NH_2)_2}_{CS\cdot S}$ [NH_2 : NH_2 : S = 1 : 2 : 4]; this separates from benzene in stout crystals, dissolves in hot alcohol or chloroform, and melts at 159—160°. The constitution of this base is shown by the formation of an *azimido*-compound $C_8H_5N_2S_2\cdot S\cdot C_6H_3{<}^{N}_{NH}{>}N$,

by the action of nitrous acid; it crystallises from alcohol or acetic acid in slender needles, melts at 186—187°, and possesses feeble acid properties.

The *metadiamidophenylic ether* of phenyldithiodiazolonethiol crystallises from dilute alcohol in bunches of stout needles. *Phenyldithiodiazolonethiol metadiamidophenylic ether* [$NH_2 : NH_2 : S \cdot C_8H_5N_2S_2 = 1 : 3 : 5$], melts at 164—165°, crystallises from alcohol in colourless needles, dissolves slightly in ether or benzene and readily in chloroform, and shows a green fluorescence in alcoholic solution. The action of nitrous acid on the base gives a brownish-red precipitate, which separates from alcohol, acetic acid, or benzene in minute crystals, melts at 156—157°, and is probably the chrysoidine compound,

$$C_8H_5N_2S_2 \cdot S \cdot C_6H_3(NH_2) \cdot N_2 \cdot C_6H_2(NH_2)_2 \cdot S \cdot C_8H_5N_2S_2.$$

Paraphenylenediamine does not appear to act on the disulphide.

Phenyldithiodiazolonethiol α-aminonaphthylic ether,

$$C_8H_5N_2S_2 \cdot S \cdot C_{10}H_6 \cdot NH_2 \ [NH_2 : S = 1 : 4],$$
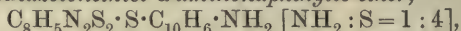
melts at 132—133°, crystallises from alcohol in bunches of white needles, dissolves in the ordinary solvents on heating, and very readily in acetone. The *hydrochloride* forms colourless needles, and when acted on with nitrous acid gives a bordeaux-red solution of the *diazo*-compound, which combines with β-naphthol to a bordeaux-red *azo-dye*, which crystallises from acetic acid or benzene in slender needles, melts at 221—222°, and gives a blue-violet solution in concentrated sulphuric acid.

Phenyldithioldiazolonethiol β-aminonaphthylic ether, [$NH_2 : S = 2 : 1$], forms colourless, silky needles, melts at 152°, and dissolves fairly readily in the ordinary solvents on heating. The *hydrochloride* forms pale yellow tablets. The *diazo*-compound combines with β-naphthol to form an *azo-dye*, which crystallises in beautiful, vermilion-red needles, and melts at 199—200°.

Unlike ethylaniline, diphenylamine does not act on the bisulphide.

<div align="right">T. M. L.</div>

Diazole Group. V. Condensation of Phenyldithiodiazolone-hydrosulphamine with Aldehydes and Ketones. By MAX BUSCH and JOS. WOLFF (*J. pr. Chem.*, 1899, [ii], 60, 197—205. Compare Abstr., 1896, i, 705).—In alcoholic solution, formaldehyde reduces the hydrosulphamine, $C_8H_5N_2S_2 \cdot S \cdot NH_2$, to the bisulphide, $S_2(C_8H_5N_2S_2)_2$, and ammonia, but does not form an aldosulphime; in aqueous solution, a viscous and partially resinous product is obtained. Similarly, acetaldehyde and œnanthaldehyde give only oily products. Furfuraldehyde, like benzaldehyde, gives a sulphime, *phenyldithiobiazolonefurfuralsulphime,* $C_8H_5N_2S_2 \cdot S \cdot N \colon CH \cdot C_4OH_3$, which melts at 152°, crystallises from a mixture of alcohol and chloroform in colourless needles, crystallises well from benzene, and dissolves slightly in alcohol or ether. When treated with alcoholic hydrogen chloride in dry ethereal solution, the sulphime is converted into *furfuraldime hydrochloride,* $C_4OH_3 \cdot CH \colon NH, HCl$, which crystallises in colourless, feathery needles, softens at 50°, and melts at 52° to a turbid, yellow oil; water decomposes it into furfuraldehyde and ammonium chloride, whilst phenylhydrazine gives furfuralphenylhydr-

azine and ammonium chloride. *Phenyldithiodiazolonemetanitrobenzal-sulphime*, $C_8H_5N_2S_2 \cdot S \cdot N \colon CH \cdot C_6H_4 \cdot NO_2$, forms microscopic needles, melts at 173—174° to a yellow oil, decomposes at 200° with frothing to a red liquid, and dissolves readily in chloroform and benzene. *Metanitrobenzaldime hydrochloride*, $NO_2 \cdot C_6H_4 \cdot CH \colon NH, HCl$, forms minute, colourless needles, melts at 249—250° to a reddish-yellow oil, and gives metanitrobenzaldehyde when acted on by water. *Phenyldithiodiazoloneanisalsulphime*, $C_8H_5N_2S_2 \cdot S \cdot N \colon CH \cdot C_6H_4 \cdot OMe$, melts at 145—146°, and crystallises from a mixture of chloroform and alcohol in colourless needles. *Anisaldime hydrochloride*, $OMe \cdot C_6H_4 \cdot CH \colon NH, HCl$, forms minute. colourless needles, softens at 170°, and melts at 175—176°. *Phenyldithiodiazolonepiperonalsulphime*,

$$C_8H_5N_2S_2 \cdot S \cdot N \colon CH \cdot C_6H_3 \colon O_2 \colon CH_2,$$
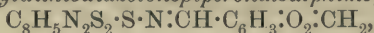
crystallises from a mixture of chloroform and alcohol in minute needles, from benzene in silky, colourless needles, and melts and decomposes at 183—184° to a reddish-brown oil. *Piperonaldime hydrochloride*, $CH \cdot O_2 \colon C_6H_3 \cdot CH \colon NH, HCl$, crystallises from benzene in minute, colourless needles, softens at 180°, and melts at about 229—230° to a dark-coloured oil. Acetone does not give the ketosulphime, but a partial reduction occurs, with separation of ammonia, and two other substances are formed; the *substance*, to which the formula $C_8H_5N_2S_2 \cdot S \cdot NH \cdot CMe_2 \cdot S \cdot C_8H_5N_2S_2$ is assigned, is only very slightly soluble in the ordinary solvents but more readily in boiling xylene, acetic acid, amylic alcohol, or chloroform; it crystallises from the latter in small, transparent, glistening prisms, melts and decomposes at 186—187° to a brown liquid, shows a normal molecular weight in naphthalene solution by the cryoscopic method, is not decomposed by boiling hydrochloric acid or caustic soda, but gives phenyldithiodiazolonebisulphide when warmed with concentrated sulphuric acid; *phenyldithiodiazoloneacetonylsulphide*,

$$C_8H_5N_2S_2 \cdot S \cdot CH_2 \cdot CO \cdot CH_3,$$
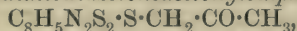
melts at 98—99°, crystallises from dilute alcohol in yellowish needles, dissolves somewhat readily in the ordinary solvents, and is indifferent towards acids and bases. Methyl ethyl ketone reduces the hydrosulphamine, with liberation of ammonia, and gives the *mercaptol*, $CMeEt(S \cdot C_8H_5N_2S_2)_2$, as a yellowish, aromatic oil; methyl propyl ketone gives a similar product. Acetophenone behaves like acetone and gives the *substance*, $C_8H_5N_2S_2 \cdot S \cdot NH \cdot CMePh \cdot S \cdot C_8H_5N_2S_2$, which crystallises from alcohol in stout prisms and melts at 158—159°.

<div align="right">T. M. L.</div>

Diazole Group. VI. Paratolyldiazolonethiol. By MAX BUSCH and H. VON BAUR-BREITENFELD (*J. pr. Chem.*, 1899, [ii], 60, 206—212). —*Paratolyldithiodiazolonethiol*, $C_7H_7 \cdot N {<}^{N=C \cdot SH}_{CS \cdot S}$, crystallises from a mixture of ether and light petroleum in yellowish needles, melts at 155°, and rapidly oxidises to the bisulphide when exposed to the air. The *benzoyl* derivative forms white needles, and melts at 100°; the *acetyl* derivative forms long, yellowish, glistening needles, and melts at 158°. The *methylic ether* crystallises from alcohol in white needles and melts at 115—116°. The *bisulphide* crystallises from a mixture of

alcohol and chloroform in minute, yellow needles, and from alcohol and benzene in clear, orange-yellow prisms, melts at 139—140°, and becomes red on prolonged exposure to the air. The thiol is reduced by sodium amalgam to paratolylthiodiazolinethiol, $C_7H_7 \cdot N {<}^{N = C \cdot SH}_{CH_2 \cdot S}$, and is oxidised by potassium permanganate to *paratolyldithiodiazolonesulphonic acid*, $C_7H_7 \cdot N {<}^{N = C \cdot SO_3H}_{CS \cdot S}$, which crystallises from a mixture of alcohol and light petroleum, cooled in a freezing mixture, in slender, glistening needles; the *potassium* and *barium* salts are described.

Paratolyldithiodiazolonehydrosulphamine, $C_7H_7 \cdot N {<}^{N = C \cdot S \cdot NH_2}_{CS \cdot S}$, prepared by the action of alcoholic ammonia on the bisulphide, melts at 150°, dissolves fairly readily in chloroform or ether, and crystallises from alcohol or benzene in slender, colourless needles; it becomes yellowish on prolonged exposure to the air, and is decomposed by acids in alcoholic solution into the bisulphide and an ammonium salt. *Paratolyldithiodiazolonethylhydrosulphamine,* $C_9H_7N_2S_2 \cdot S \cdot NHEt$, forms slender, white needles, and melts at 118—119°; the *dimethylhydrosulphamine,* $C_9H_7N_2S_2 \cdot S \cdot NMe_2$, forms slender, white needles, and melts at 85°, and readily decomposes into the bisulphide and the amine; diamylamine has a reducing action, and gives only the diamylamine salt of the original thiol.

Paratolyldithiodiazolonethiol paramidophenylic ether,
$$C_9H_7N_2S_2 \cdot S \cdot C_6H_4 \cdot NH_2 \ [NH_2 : S = 1 : 4],$$
separates from dilute acetic acid in stout, glistening, slightly yellowish crystals, dissolves readily in benzene or chloroform, less readily in alcohol or ether, and melts at 173°; the *hydrochloride* forms white, glistening needles; the *platinochloride* is an orange-yellow, micro-crystalline powder, and the diazo-compound forms a red *azo-dye* with β-naphthol.

Paratolyldithiodiazolonethiol methylamidophenylic ether,
$$C_9H_7N_2S_2 \cdot S \cdot C_6H_4 \cdot NMe,$$
melts at 184°, crystallises from alcohol in white needles, dissolves in benzene, chloroform, or acetic acid, and slightly in ether or ethylic acetate; the *nitrosamine* forms minute needles, melts at about 127°, and gives Liebermann's reaction.   T. M. L.

Diazole Group. VII. Orthotolyl- and α- and β-Naphthyl-di-thiodiazolonethiols. By MAX BUSCH and HEINRICH MÜNKER (*J. pr. Chem.*, 1899, [ii], 60, 212—216).—*Orthotolyldithiodiazolonethiol,* $C_7H_7 \cdot N {<}^{N = C \cdot SH}_{CS \cdot S}$, forms a white, crystalline precipitate, and dissolves readily in alcohol, ether, benzene, or chloroform. The *methylic ether* forms white needles and melts at 98°. The *bisulphide* crystallises from chloroform in beautiful, yellow needles or flakes. *Orthotolyldithiodiazolonethiol paramidophenylic ether,* $C_9H_7N_2S_2 \cdot S \cdot C_6H_4 \cdot NH_2$, forms white needles and melts at 128°.

α-Naphthyldithiodiazolonethiol, $C_{10}H_7 \cdot N {<}^{N = C \cdot SH}_{CS \cdot S}$, melts at 127°,

The *benzoyl* derivative crystallises from alcohol in minute, yellowish needles and melts at 146°. The *bisulphide* crystallises from a mixture of chloroform and alcohol in beautiful, yellow flakes and melts at 228°.

β-Naphthyldithiodiazolonethiol crystallises from benzene in colourless needles and melts at 160°. The *methylic* ether crystallises from alcohol in white needles and melts at 112°. The *bisulphide* forms yellow needles and melts at 188°. *Naphthyldithiodiazolonesulphonic acid*,

$$C_{10}H_7 \cdot N \underset{CS \cdot S}{\overset{N=C \cdot SO_3H}{<}}$$

, forms brownish flakes, and gives crystalline

potassium, barium, and *lead* salts.

Orthoanisyldithiodiazolonethiol, $OMe \cdot C_6H_4 \cdot N \underset{CS \cdot S}{\overset{N=C \cdot SH}{<}}$, crystallises

from a mixture of benzene and light petroleum in well-formed, transparent, yellowish prisms, and melts at 119—120°. The *bisulphide* forms yellow needles and melts at 174—175°.   T. M. L.

Diazole Group. VIII. Action of Ammonia and Aniline on Phenylmethylthiodiazoline Bisulphide. By MAX BUSCH (*J. pr. Chem.*, 1899, [ii], **60**, 216—217. Compare Abstr., 1896, i, 190).— Phenylmethylthiodiazoline bisulphide, when treated with alcoholic ammonia, gives sulphur, phenylthiosemicarbazide, and the ammonium derivative of phenylmethyldiazolinethiol. Aniline similarly gives sulphur, diphenylthiosemicarbazide, and the aniline derivative of the thiol.   T. M. L.

Diazole Group. IX. Phenyldithiocarbazinic Acid and Benzoic Chloride. By MAX BUSCH and J. BECKER (*J. pr. Chem.*, 1899, [ii], **60**, 217—219).—*Ethylic phenyldithiocarbazinate,*
$$NHPh \cdot NH \cdot NH \cdot CS \cdot SEt,$$
crystallises from alcohol in beautiful, transparent prisms and melts at 127°. The *benzylic* salt crystallises from benzene in splendid, transparent prisms and melts at 164°. The benzoyl derivative cannot be isolated, as it immediately loses water and gives diphenylisodithio-

diazolone, $NPh \underset{CPh \cdot S}{\overset{N——CS}{<}}$ (Abstr., 1896, i, 190) ; a second product

of the action of benzoic chloride on phenyldithiocarbazinic acid is *dibenzophenylhydrazide*, $NPh Bz \cdot NHBz$, which crystallises from alcohol in glistening, white needles and melts at 177—178°.   T. M. L.

Diazole Group. X. Diazolines from Paratolyldithiocarbazinic Acid and its Ethereal Salts. By MAX BUSCH [and E. LINGENBRINK] (*J. pr. Chem.*, 1899, [ii], **60**, 219—225).—*Methylic paratolyldithiocarbazinate*, $C_7H_7 \cdot NH \cdot NH \cdot CS \cdot SMe$, forms glistening, colourless needles and melts at 149°. The *ethylic* salt crystallises from alcohol in well-formed, transparent prisms and melts at 128°. The *benzylic* salt forms colourless needles, dissolves slightly in alcohol, and readily in ether or benzene, and melts at 146°. The action of ethylenic dibromide on the potassium salt does not give the ethylenic salt, but a ring compound, *paratolylpentahydro*-1 : 2 : 4-*diazthine*,

$$C_7H_7 \cdot N \underset{CH_2 \cdot CH}{\overset{NH——CS}{<}} S,$$
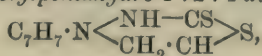
which melts at 124°, separates from a mixture of benzene and light

petroleum in bunches of pointed crystals, and dissolves fairly readily in the ordinary solvents, with the exception of light petroleum; alcoholic ferric chloride gives a dark blue coloration, and a black, amorphous mass is precipitated on adding water to the solution; the colour disappears on adding alkali.

Formaldehyde condenses with the potassium salt to form *paratolyl-thiodiazolinethiol*, $C_7H_7 \cdot N \underset{CH_2 \cdot S}{\overset{N = C \cdot SH}{<}}$, which crystallises from benzene in beautiful, white flakes, melts at 80°, but at 103—105° when kept overnight in a desiccator, dissolves readily in alcohol, benzene, ether, or chloroform, and slightly in light petroleum, and dissolves in cold caustic alkalis, but is decomposed, on warming, into the aldehyde and carbazinic acid. The *bisulphide* crystallises in orange-red needles on adding alcohol to a solution in chloroform, and melts at 102° to a red oil which at once becomes yellow owing to the decomposition of the bisulphide into the thiol, and the isodithiodiaz-olone. *Paratolylisodithiodiazolone*, $C_7H_7 \cdot N \underset{CH \cdot S}{\overset{N - CS}{<}}$, is formed by decomposition of the bisulphide in chloroform solution at the ordinary temperature and rapidly on warming; it crystallises in bunches of yellow needles, melts at 198°, and dissolves only sparingly in the ordinary solvents; the *methiodide* crystallises from chloroform in long, yellow needles, and when treated with alkalis, gives a yellowish-brown, oily base.

Paratolylmethylthiodiazolinethiol, $C_7H_7 \cdot N \underset{CHMe \cdot S}{\overset{N = C \cdot SH}{<}}$, prepared by the condensation of acetaldehyde with paratolylcarbazinic acid, crystallises from benzene in beautiful, colourless, transparent prisms, and melts at 143°. The *bisulphide* crystallises from a mixture of alcohol and chloroform in splendid, glistening, orange-yellow flakes, and melts at 123°; it is fairly stable, but decomposes on heating at 100°.

Paratolylmethylisodithiodiazolone, $C_7H_7 \cdot N \underset{CMe \cdot S}{\overset{N - CS}{<}}$, crystallises from a mixture of chloroform and alcohol in silvery, grey flakes and melts at 216°. When heated with aniline, the bisulphide gives sulphur and paratolylphenylsemicarbazide.

Paratolylmethylthiodiazolinethiol methylic ether,

$$C_7H_7 \cdot N \underset{CHMe \cdot S}{\overset{N = C \cdot SMe}{<}},$$
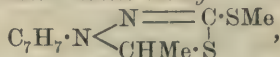
prepared by condensation of acetaldehyde with methylic paratolyl-dithiocarbazinate, crystallises in colourless, glistening needles or small flakes, melts at 50°, and dissolves readily in the ordinary solvents. Benzaldehyde condenses similarly to *tolylphenylthiodiazolinethiol methylic ether*, $C_7H_7 \cdot N \underset{CHPh \cdot S}{\overset{N = C \cdot SMe}{<}}$, which crystallises in stout, glistening, white needles and melts at 99°. The corresponding *ethylic* salt crystallises similarly and melts at 89°; the *benzylic* salt melts at 105°, is much less soluble in alcohol, and crystallises in hair-like needles. T. M. L.

Diazole Group. XI. Orthanisyl- and α- and β-Naphthyl-dithio-carbazinic Acids and their Derivatives. By MAX BUSCH and FRIEDRICH BEST (*J. pr. Chem.*, 1899, [ii], **60**, 225—232).—*Potassium orthanisyldithiocarbazinate*, OMe·C₆H₄·NH·NH·CS·SK, crystallises in white, microscopic flakes. With ethylenic bromide, it forms *orthanisyl-pentahydro*-1 : 3 : 5-*dithiodiazine*, $OMe \cdot C_6H_4 \cdot N {<}^{NH-CS}_{CH_2 \cdot CH_2}{>}S$; this crystallises from dilute alcohol in long, pointed forms, which, like the solution, become green on exposure to the air, and from light petroleum in stout, white needles, dissolves very readily in all other solvents, and melts at 85—86° ; the *acetyl* derivative separates from benzene in stout, white crystals, and melts at 150° ; the *hydrochloride* forms white needles and melts at 163—164°.

Orthanisylmethylthiodiazolinethiol, $OMe \cdot C_6H_4 \cdot N {<}^{N=C \cdot SH}_{CHMe \cdot S}$, crystallises from benzene in beautiful, large, yellowish prisms, melts at 149°, and dissolves readily in alcohol.

Potassium α-naphthyldithiocarbazinate, C₁₀H₇·NH·NH·CS·SK, melts at 118°, dissolves readily in alcohol or water, and crystallises in white flakes, but soon becomes yellow on exposure to the air. The *methylic* salt melts with decomposition at 160°, crystallises in white needles, has a characteristic odour suggestive of fresh mushrooms, and gradually becomes blue-grey on exposure to air. The *ethylic* salt is similar, and melts at 124°. The *benzylic* salt melts at 127° and crystallises from alcohol in white needles. α-*Naphthylpentahydro*-1 : 3 : 5-*dithiodiazine*, $C_{10}H_7 \cdot N {<}^{NH-CS}_{CH_2 \cdot CH_2}{>}S$, separates from benzene in stout, yellowish crystals, melts at 148°, dissolves in hot alcohol, and soon becomes green unless quite pure ; the *hydrochloride* forms glistening, yellowish needles, melts at 182—183°, and is decomposed by water.

α-*Naphthylphenyldithioisodiazoline,* $C_{10}H_7 \cdot N {<}^{N-CS}_{CPh \cdot S}$, prepared by the action of benzoic chloride on the carbazinic acid, crystallises from a mixture of chloroform and alcohol in bunches of golden-yellow needles, melts at 207°, is only dissolved largely by hot chloroform, and is hydrolysed by caustic alkalis to benzoic acid and α-naphthyldithio-carbazinic acid.

No condensation could be effected with formaldehyde, but acetalde-hyde gave α-*naphthylmethylthiodiazolinethiol,* $C_{10}H_7 \cdot N {<}^{N=C \cdot SH}_{CHMe \cdot S}$; this crystallises from a mixture of ether and light petroleum in transparent, yellowish, efflorescent needles, dissolves readily in alcohol, benzene, or chloroform, and slightly in light petroleum, and melts at 164°. The *bisulphide* was precipitated, on adding ferric chloride to the alcoholic solution, in yellow flocks, but was obtained as a yellow oil on attempting to recrystallise it. The *methylic ether* melts at 108°, crystallises from light petroleum in glistening, trans-parent, well-formed needles or prisms, and dissolves readily in alcohol, ether, or benzene.

Benzaldehyde does not condense with methylic α-naphthyldithio-carbazinate at 100°, and at 120° a non-crystalline product is obtained.

Potassium β-naphthyldithiocarbazinate, $C_{10}H_7 \cdot NH \cdot NH \cdot CS \cdot SK$, dissolves readily in water, crystallises from alcohol in glistening needles, and melts at 112°. The *methylic* salt melts at 143—144°, crystallises in small, white needles, and resembles the α-compound. The *ethylic* salt melts at 142—143°. The *benzylic* salt melts at 171°. The *β-naphthyl-pentahydrodithiodiazine*, $C_{10}H_7 \cdot N {<}_{CH_2 \cdot CH_2}^{NH—CS} {>} S$, is very sensitive to oxygen and the solutions immediately become bluish-green; the *hydrochloride* separates from alcohol in yellow needles and melts at 200—201°.

β-Naphthylphenylisodithiodiazolone, $C_{10}H_7 \cdot N {<}_{CPh \cdot S}^{N—CS}$, separates from a mixture of chloroform and alcohol in yellow, radiating needles, melts at 212—213°, and closely resembles the α-compound.

β-Naphthylthiodiazolinethiol, $C_{10}H_7 \cdot N {<}_{CH_2 \cdot S}^{N=C \cdot SH}$, crystallises from benzene in yellowish prisms and melts at 115°.

β-Naphthylmethylthiodiazolinethiol, $C_{10}H_7 \cdot N {<}_{CHMe \cdot S}^{N=C \cdot SH}$, melts at 164—165°, and crystallises from benzene in clear, yellowish prisms; it dissolves in cold caustic soda, but on warming is decomposed with separation of acetaldehyde.   T. M. L.

Diazole Group. XII. Phenyldimethylthiodiazolinethiol. By MAX BUSCH and ALFRED STERN (*J. pr. Chem.*, 1899, [ii], **60**, 233—235). — *Phenyldimethylthiodiazolinethiol*, $NPh {<}_{CMe_2 \cdot S}^{N=C \cdot SH}$, formed by condensation of acetone with phenyldithiocarbazinic acid, melts at 135—136°, separates from a mixture of benzene and light petroleum in large, well-formed crystals, and dissolves readily in ordinary solvents. The action of iodine on the potassium salt breaks the ring and gives the bisulphide of phenylthiocarbazinic acid (Abstr., 1896, i, 677), and not the bisulphide of the thiol; similarly, methylic iodide does not give the methylic salt of the thiol, but methylic phenyl-dithiocarbazinate; the dialkylated diazoline ring is therefore somewhat unstable.

Phenylmethylethylthiodiazolinethiol, $NPh {<}_{CMeEt \cdot S}^{N=C \cdot SH}$, crystallises from a mixture of benzene and light petroleum in white needles, melts with frothing at 158°, and in solubility resembles the dimethyl derivative.

No condensation occurs in the case of acetophenone or when the etheric salts are used in place of the carbazinic acid.   T. M. L.

Diazole Group. XIII. Formation of Diazoles from Phenyl-carbazinic and Phenylthiocarbazinic Acids. By MAX BUSCH and ALFRED STERN (*J. pr. Chem.*, 1899, [ii], **60**, 235—243. Compare Fischer, Abstr., 1878, 307).—*Potassium phenylcarbazinate* crystallises from alcohol in beautiful, glistening needles and melts with decomposition at 243°; it is immediately decomposed by mineral acids with

liberation of carbonic anhydride, but is fairly stable in the dry state ; the etheric salts could not be prepared by the action of alkyl iodides on the potassium salt, as a similar decomposition of the acid took place. The action of phosgene on the potassium salt led to the formation of diphenylurazine, and not of the phenylhydroxydiazolone, $NPh\begin{smallmatrix} N=C \cdot OH \\ CO \cdot O \end{smallmatrix}$, which was expected. The action of acetaldehyde caused the decomposition of the acid and led to the formation of phenylethylidenehydrazine. Carbon bisulphide gave phenyldithiodiazolonethiol by interaction with the phenylhydrazine liberated by the decomposition of the carbazinic acid. Diazolones can, however, be prepared from the stable ethylic salt of phenylcarbazinic acid (Heller, Abstr., 1891, 1212).

Ethylic chlorocarbonylphenylcarbazinate, COCl·NPh·NH·COOEt, prepared by the action of carbonyl chloride on ethylic phenylcarbazinate, melts at 101°, crystallises from light petroleum in glistening, white needles, and dissolves readily in the ordinary solvents. By distillation, or by the action of alkalis, it loses hydrogen chloride, and gives *ethoxyphenyldiazolone*, $NPh\begin{smallmatrix} N=C \cdot OEt \\ CO \cdot O \end{smallmatrix}$; this crystallises from alcohol in beautiful, large, clear prisms, dissolves readily in alcohol, ether, benzene, or chloroform, slightly in light petroleum, and melts at 72°. *Ethylic chlorothiocarbonylphenylcarbazinate*, CSCl·NPh·NH·COOEt, separates from a mixture of benzene and light petroleum in stout, colourless crystals, dissolves readily in most solvents, and melts at 116°, giving off bubbles of gas. By the action of alkali, it yields *ethoxyphenylpseudothiodiazolone*, $NPh\begin{smallmatrix} N=C \cdot OEt \\ CS \cdot O \end{smallmatrix}$; this is less stable than the corresponding oxygen compound, and decomposes when heated to the boiling point ; it crystallises from alcohol in large, white needles and melts at 29°. Ethylic phenylcarbazinate does not condense with acetaldehyde at the ordinary temperature, and on heating decomposition occurs.

Potassium phenylthiocarbazinate, NHPh·NH·CO·SK (compare Heller, *loc. cit.*), separates from alcohol in stout, white crystals containing 1 mol. of alcohol. The *bisulphide* is an insoluble, white compound. Phenylethylidenehydrazine is produced when acetaldehyde acts on potassium phenylthiocarbazinate, owing to the decomposition of the acid ; the etheric salts can, however, be prepared by the action of alkylic iodides on the potassium salt. The *methylic* salt crystallises from alcohol in beautiful, white needles, dissolves readily in the ordinary solvents, except light petroleum, and melts at 152°. The *ethylic* salt forms white needles and melts at 113°. The *benzylic* salt is less soluble in alcohol, and crystallises in slender, white needles ; it melts at 170°. By the action of carbonyl chloride on the methylic salt, *phenyldiazolonethiol methylic ether*, $C_6H_5 \cdot N\begin{smallmatrix} N=C \cdot SMe \\ CO \cdot O \end{smallmatrix}$, is produced ; it melts at 55—56°, dissolves readily in alcohol, benzene, ether, or chloroform, and slightly in light petroleum, but not in water.

T. M. L.

Triazan Derivatives. By HUGO VOSWINCKEL (*Ber.*, 1899, **32**, 2481—2492 ; 2770).—*Phenylethylideneoxycyclotriazan*, $NPh{<}^{NO}_{N}{>}CHMe$,

$NPh{<}^{N(OH)}_{N}{>}CMe$, or $NPh{<}^{NH \cdot O}_{N-N}$, is produced by adding an aqueous solution of aldehyde-ammonia to an alcoholic solution of phenylnitrosohydrazine and heating the mixture for a few minutes on the water-bath ; ammonia is evolved, and the residue, after distilling off the alcohol, is crystallised from dilute alcohol. It forms flexible, orange needles, and melts at 116°, the melting point being perceptibly influenced by the rate of heating. It is soluble in ether, benzene, or hot water, and is reprecipitated by acids from its solution in dilute alkalis ; it is volatile in steam and distils without decomposition. The *sodium* derivative is formed by adding an excess of sodium hydroxide to a solution of the condensation product in absolute alcohol or in dilute caustic soda ; it separates in light yellow needles, which are soluble in water, alcohol, or hot acetone, but not in ether or benzene ; it detonates on heating.

The *methyl* derivative, $NPh{<}^{NMe \cdot O}_{N-N}$, obtained by heating an aqueous solution of the preceding compound with methylic iodide, crystallises in dark orange needles and melts at 90° ; it is soluble in the ordinary organic solvents.

Phenyldimethylcyclomethylenetriazan hydrochloride, $NPh{<}^{NMe}_{NH}{>}CHMe,HCl$, produced by reducing the preceding compound with stannous chloride, crystallises from alcohol in pale yellow, highly refractive needles melting at 281° ; it is very soluble in water and does not yield condensation products with benzaldehyde. The base is a colourless oil becoming brown on exposure to air. When the reduction is carried further, another base is formed, which, in all probability, has the constitution $NH_2 \cdot NPh \cdot NMe \cdot CH_2Me$; it condenses readily with benzaldehyde.

Phenylmethyloxycyclomethylenetriazan, $NPh{<}^{N(OH)}_{NH}{>}CHMe$, obtained by reducing the original condensation product with aqueous ammonium sulphide or stannous chloride, dissolves in alcohol or benzene, but not in water or dry ether, crystallises in leaflets, and melts at 130° ; by oxidising agents, such as nitrous acid, it is reconverted into the parent substance, and this change is also effected by repeated crystallisation from dilute alcohol. The compound is basic, and its *hydrochloride* forms colourless prisms and melts at 174°.

Chlorophenylmethyloxycyclomethylenetriazan hydrochloride separates in reddish-white needles from a solution of phenylethylideneoxycyclotriazan in concentrated hydrochloric acid ; it melts at 174°. The *base*, $C_6H_4Cl \cdot N{<}^{N(OH)}_{NH}{>}CHMe$, is readily soluble in alcohol, ether, or benzene, but insoluble in water ; it melts at 131°.

*Chlorophenylethylideneoxycyclotriazan*, whose constitution may be

represented by $C_6H_4Cl \cdot N{<}^{NO}_{N}{>}CHMe$, or the other tautomeric formulæ corresponding with those of phenylethylideneoxycyclotriazan, is obtained by boiling the preceding compound with water or by crystallising from hot alcohol; it forms orange needles, melts at 189°, dissolves in alcohol, ether, benzene, or dilute alkalis, but not in water; reducing agents reconvert it into the parent substance.

The corresponding bromo-compounds, $C_8H_{10}ON_3Br$ and $C_8H_8ON_3Br$, melt at 128° and 195° respectively.

Phenylmethylcyclomethylenetriazan hydrochloride is prepared by reducing phenylmethyloxycyclomethylenetriazan with stannous chloride; it crystallises in silky needles containing $1H_2O$, and melts at 140°; when heated to 105°, it becomes anhydrous and then melts at 205°.

The base, $NPh{<}^{NH}_{NH}{>}CHMe$, is an oil; its salts can be decomposed by soda or potash, but not by ammonia.

Phenylethyltriazan hydrochloride, $NH_2 \cdot NPh \cdot NH \cdot CH_2Me, HCl$, obtained on reducing phenylmethoxycyclomethylenetriazan hydrochloride with stannous chloride, is separated from the admixed phenylhydrazine hydrochloride by fractional crystallisation; the hydrochloride of the triazan is the more soluble; it crystallises in colourless needles and melts at 185°. The base is an easily decomposable oil; its salts are not decomposed by ammonia, and with dilute acids intense reddish colorations are developed. The *benzylidene* compound,

$$CHPh{:}N \cdot NPh \cdot NH \cdot CH_2Me,$$
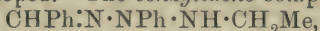
produced by mixing together benzaldehyde and the base at ordinary temperatures, crystallises in pale yellow needles which redden on exposure to air; it melts at 163°.

Phenyltriazan hydrochloride, $NH_2 \cdot NPh \cdot NH_2, HCl$, is separated by fractional crystallisation from the mixture of hydrochlorides obtained by the ultimate reduction of phenylethylideneoxycyclotriazan with ammonium sulphide; it crystallises in white needles and melts at 220°.

Paratolylethylideneoxycyclotriazan, prepared by condensing paratolylnitrosohydrazine with aldehyde ammonia, crystallises in flexible, pale orange needles and melts at 135°; it closely resembles its lower homologue.

Paratolylmethyloxycyclomethylenetriazan, obtained by reducing the preceding compound with ammonium sulphide, crystallises in silvery, white needles and melts at 122°; it is soluble in the ordinary organic solvents, but not in water.   G. T. M.

Alkaloids contained in Anagyris Fœtida. By MAX KLOSTERMANN (*Chem. Centr.*, 1899, i, 1130; from *Diss. Marburg*, 1898. Compare Abstr., 1896, i, 657).—By evaporating the alcoholic extract of the seeds of *Anagyris fœtida*, precipitating the aqueous solution with lead acetate, and decomposing the precipitate with hydrogen sulphide, a mixture of cytisine and anagyrine is obtained, from which the latter may be separated by dissolving in water acidified with hydrochloric acid and precipitating as the mercurichloride, whilst the former is isolated by making the solution alkaline and extracting with chloroform.

Cytisine, $C_{11}H_{14}ON_2$, crystallises from light petroleum in white needles and melts at 152—153°. The *nitrate*, $C_{11}H_{14}ON_2,HNO_3 + H_2O$, crystallises from a mixture of alcohol and ether in long, white needles, and has specific rotatory power $[a]_D - 81° 29'$ when $p = 3·5112$. The platinochloride, $(C_{11}H_{14}ON_2)_2,H_2PtCl_6$, crystallises in yellow needles. The aurichloride, $C_{11}H_{14}ON_2,HAuCl_4$, crystallises from water in yellow needles and melts at 220°. *Anagyrine mercurichloride*, $C_{15}H_{22}ON_2,HHgCl_3$, separates from hot water in nodular crystals and melts at 233—234°. Anagyrine is prepared from the preceding compound by decomposing it with hydrogen sulphide and treating with alkali, but could not be obtained in a crystalline form. The *hydrochloride*, $C_{15}H_{22}ON_2,HCl + H_2O$, crystallises in rhombic plates, is easily soluble in water or alcohol, insoluble in ether or chloroform, and has a specific rotatory power $[a]_D - 142° 28'$ when $p = 1·8140$. The *hydrobromide*, $C_{15}H_{22}ON_2,HBr + H_2O$, has properties similar to those of the hydrochloride and melts above 235°. The *nitrate*, $C_{15}H_{22}ON_2,HNO_3 + H_2O$, crystallises from a mixture of alcohol and ether in long, white needles, and has specific rotatory power $[a]_D - 126° 2'$ when $p = 1·00$. The platinochloride, $C_{15}H_{22}ON_2,H_2PtCl_6 + 1\frac{1}{2}H_2O$, forms ruby-red needles, does not melt below 235°, and is slightly soluble in water. The aurichloride, $C_{15}H_{22}ON_2,HAuCl_4$, forms a bulky, crystalline precipitate and melts at 210—211°. *Anagyrine methiodide*, $C_{15}H_{22}ON_2,MeI$, crystallises from methylic alcohol in snow-white needles and melts above 235°. The *platinochloride*, $C_{15}H_{22}ON_2,MeI,H_2PtCl_6 + H_2O$, crystallises from dilute hydrochloric acid in yellowish-red needles and melts above 235°. The results of experiments on the introduction of methyl groups, together with other evidence, indicate that anagyrine is a bitertiary base. *Dibromanagyrine hydrobromide*, $C_{15}H_{20}ON_2Br_2,HBr$, prepared by treating an alcoholic solution of anagyrine hydrobromide with bromine and heating the resulting precipitate with alcohol, crystallises in silky, white needles, melts above 235°, and is easily soluble in alcohol or water. *Dibromanagyrine platinochloride*, $C_{15}H_{20}ON_2Br_2,H_2PtCl_6$, forms reddish-yellow needles and melts above 235°. The *aurichloride* separates in reddish-yellow needles and melts at 223°. When the properties of anagyrine are compared with those of cytisine, it is evident that the former is probably butylcytisine.　　　　　　　　　　　　　　E. W. W.

Isomerism in the Cinchonine Group. By ZDENKO H. SKRAUP (*Monatsh.*, 1889, **20**, 571—584).—A critical examination of the alleged isomerides of cinchonine. Hesse's α- and β-isocinchonine (Abstr., 1893, i, 677) are easily separated in the form of the dihydriodides, that of α-isocinchonine being easily soluble and that of β-isocinchonine almost insoluble in cold water. These two, and the two isomerides δ- and ε-cinchonine obtained by Cordier (*Monatsh.*, 1898, **19**, 472) from *hydrobromocinchonine*, are well characterised by their specific rotatory powers, and there can be no doubt that they are actual isomerides of cinchonine.

Cordier's tautocinchonine (*loc. cit.*) is very similar to cinchonine, but the differences in the solubilities of the two bases in alcohol and of their sulphates in water point to tautocinchonine being a true isomeride of cinchonine. Hesse's "apocinchonine," "apoisocincho-

nine" and "isoapocinchonine" are one and the same compound, which is identical with Lippmann and Fleissner's allocinchonine (Abstr., 1893, i, 738). Allocinchonine is well characterised by the sparing solubility of its normal sulphate in water (1 part in 120 at 20°). The "cinchonifine" of Jungfleisch and Léger (Abstr., 1888, 380) is probably cinchotine, with which Hesse's pseudocinchonine is identical (von Arlt, this vol., i, 962).

After a close comparison of the sulphate and platinochloride of Hesse's homocinchonine with the corresponding compounds of cinchonine, the author comes to the opinion that the two bases are identical.

Jungfleisch and Léger (Abstr., 1892, 1253) have stated that Hesse's diapocinchonine is a mixture of α- and β-isocinchonine. This is disputed by Hesse (loc. cit.), but now confirmed by the author, who has separated α- and β-isocinchonine from "diapocinchonine" by means of the dihydriodides.

The directions given by Pum (Abstr., 1893, i, 181) for the preparation of β- and γ-cinchonine were followed, but the substance obtained was allocinchonine.

Hydrochlorapocinchonine and hydrochlorapoisocinchonine were prepared according to Hesse's method. From a redetermination of the solubilities of the bases and their salts, there is no doubt that they are both identical with hydrochlorocinchonine. This, however, differs so much from hydrochloro-α-isocinchonine that there is no possibility that they are identical. R. H. P.

Molecular Transformations: the Transformation of Cinchonine into α-Isocinchonine. By ZDENKO H. SKRAUP (Monatsh., 1899, 20, 585—616).—If hydrochloric, hydrobromic, or hydriodic acid acts on cinchonine at the ordinary temperature, a portion of the cinchonine is transformed into α-isocinchinone and another portion converted into an additive compound. In this paper, the data of a large number of experiments with acids of ten and fourteen times normal strength and the quantities of α-isocinchonine and the addition products thus formed at different intervals are given. Much time is taken for the completion of the reactions, but only the results obtained at the beginning of the actions are of any value, since a secondary reaction between the α-isocinchonine and the acid interferes after a short time. The velocities with which hydriodic, hydrobromic, and hydrochloric acids form the additive compounds are in the proportion of 200,000 : 400 : 1. The quantities of cinchonine transformed into α-isocinchonine in the same time by these acids are in the proportion of 10 : 2·6 : 1, and the ratio of the amount of cinchonine transformed into α-isocinchonine to that converted into an additive compound varies for each acid, but is independent of the concentration, time, or temperature.

This transformation cannot be referred to the action of ions, for the amounts of cinchonine transformed into α-isocinchonine by the three acids bear no proportion to their electrical conductivities. Further, it is noteworthy that nitric acid will not effect the transformation. The results show that this molecular transformation is dependent on

a second reaction taking place at the same time (compare the author's views on the conversion of maleic acid into fumaric acid (Abstr., 1891, 1338).

Cinchonine dinitrate, $C_{19}H_{22}N_2O,(HNO_3)_2$, is formed when a solution of cinchonine hydrogen sulphate is treated with barium nitrate, filtered, and evaporated. On the addition of alcohol, the salt crystallises out in the form of large, lustrous prisms.   R. H. P.

Pseudocinchonine and the Behaviour of Hydrochlorocinchonine. By F. von ARLT (*Monatsh.*, 1899, **20**, 425—449).— This is a repetition of Hesse's work on the same subject (Abstr., 1893, i, 677). The author treats cinchonine dihydrochloride with hydrochloric acid of sp. gr. 1·160 at 100° (instead of at 80°). About 29 per cent. of the cinchonine is converted into hydrochlorocinchonine dihydrochloride, which crystallises out of the solution. The mother liquor is treated according to Hesse's method with ammonia and ether. 64 per cent. of the cinchonine is thus obtained as pseudocinchonine and about 8 per cent. as a mixture of bases easily soluble in ether. The crude pseudocinchonine is purified by treatment of its crude hydrochloride with alcoholic potash, reconversion of the base into the hydrochloride, and crystallisation of the latter. By neutralising and crystallising the mother liquor, Hesse's apoisocinchonine can be obtained. From its melting point (214—217°) and the solubility (1 pt. in 117·07 pts. of water) of its sulphate $(C_{19}H_{22}ON_2)_2,H_2SO_4 + 1\frac{1}{2}H_2O$, there is little doubt of its identity with Lippmann and Fleissner's allocinchonine (Abstr., 1893, i, 738).

The mother liquor obtained after treating the crude pseudo-cinchonine hydrochloride with alcoholic potash yields another alkaloid. This melts at 141°, has a specific rotatory power in alcoholic solution $(p=1)$ $[a]_D + 140\cdot7°$ at 20°, and is probably identical with Cordier's δ-cinchonine (*Monatsh.*, 1898, **19**, 473).

Pure pseudocinchonine is proved to be identical with cinchotine. It melts at 265—267·5° and thus agrees with the melting point of cinchotine found by Forst and Böhringer (Abstr., 1881, 620, and 830) and by Pum (*Monatsh.*, 1895, **16**, 70).

The solubility of the base in alcohol is 1 pt. in 218·9 pts., while that of cinchotine is 1 pt. in 221·5 pts. The hydrochloride (melting at 216°), the hydriodide (melting at 127°), and the dihydriodide (melting at 258°) are identical with the corresponding compounds of cinchotine. *Cinchotine methiodide*, $C_{19}H_{24}ON_2,MeI$, forms hard, white prisms melting at 244—246°. The *hydriodide* of *cinchotine methiodide*, $C_{19}H_{24}ON_2,MeI,HI$, crystallises in compact, yellow prisms which turn brown at 221° and decompose at 227—229°. It does not yield the methiodide on treatment with ammonia or sodium carbonate,

Cinchotine, when oxidised by potassium permanganate in acid solution, yields formic acid and a dark brown syrup, which, however, contains no cinchotenine.

The author's treatment of cinchonine dihydrochloride yields a much smaller proportion of the bases easily soluble in ether than Hesse obtained. The formation of α-isocinchonine in this manner is confirmed by the author, who also finds small quantities of β-isocin-

chonine (probably formed by the action of the hydrochloric acid at the higher temperature on α-isocinchonine).

Hesse's work on the action of alcoholic potash on hydrochloro-cinchonine has also been repeated. α-Isocinchonine is separated from the mixture of three bases thus obtained by its solubility in ether. The two bases insoluble in ether are fractionated by crystallisation from alcohol. The one melts at 246°, has a specific rotatory power when dissolved in two volumes of alcohol and one of chloroform ($p = 3$) $[a]_{D20°} + 215\cdot51°$, dissolves in $120\cdot4$ pts. of water, and is either cinchonine, or more probably Cordier's tautocinchonine (*loc. cit.*). Its sulphate, $(C_{19}H_{22}ON_2)_2,H_2SO_4 + 2H_2O$, dissolves in $61\cdot18$ pts. of water. The other base agrees in its properties with Hesse's apoisocinchonine and Lippmann and Fleissner's allocinchonine, with the exception that its sulphate has the composition $(C_{19}H_{22}ON_2),H_2SO_4 + 4H_2O$.

Similar results were obtained by hydrolysing hydrochlorocinchonine with alcoholic silver nitrate. The proportion, however, of the bases insoluble in ether is in this case much larger. R. H. P.

Cocaine. By FRITZ GÜNTHER (*Chem. Centr.*, 1899, i, 848; from *Ber. pharm. Ges.*, 9, 38—43. Compare *Pharm. Centr.-Halle*, 39, 1).— Mac-Lagan's reaction for cocaine is useless for the valuation of the commercial article, and is most probably dependent on the presence of another base, for pure cocaine hydrochloride, when dissolved in 1000 parts of water, does not separate in a crystalline form on the addition of ammonia. A considerable quantity of a base which melts at 110—111° and, according to Salkowski, acts physiologically like cocaine itself, has been isolated from cocaine. Mixtures of this base with cocaine dissolve like a homogeneous compound, and both bases crystallise from such solutions in apparently perfectly homogeneous, transparent prisms. From mixtures containing larger proportions of cocaine, the bases may be separated directly, although with difficulty, by means of light petroleum; a better separation is effected by dissolving in alcohol, neutralising with a solution of hydrogen chloride in alcohol, and then precipitating the hydrochloride with ether. The mother liquor then contains a mixture of bases from which the one of higher melting point may be isolated by means of light petroleum. At 20°, this base requires $2500 - 3000$ parts of water for solution (cocaine 704), and its solubility in other solvents is also less than that of cocaine. It is almost as strongly lævo-rotatory as cocaine, forms an aurichloride and picrate which cannot be distinguished from those of cocaine even under the microscope, and yields benzoic acid when decomposed by hydrochloric acid of sp. gr. $1\cdot1$. The results of analysis agree with the composition of a methylcocaine, and the compound is possibly an ethylbenzoylecgonine in which the hydrogen of the carboxyl group is replaced by ethyl. It is isomeric, but not identical, with cocethyline, which also gives Mac-Lagan's reaction. When treated with methylic alcohol, the benzoyl-ecgonine prepared from this base yields methylbenzoylecgonine melting at 101°. The methylic alcohol, however, even after the most careful purification, was found to contain traces of ethylic alcohol

which easily condenses with benzoylecgonine, for even when obtained from the purest cocaine, benzoylecgonine was found also to yield bases of higher melting point when treated with this alcohol. It is probably for this reason, too, that the synthetically prepared commercial cocaine also gives MacLagan's reaction. A solution of 0·1 gram of cocaine hydrochloride in 85 c.c. of water should remain clear when 0·2 c.c. of ammonia solution is added. E. W. W.

Damascenine. By HERBERT POMMEREHNE (*Arch. Pharm.*, 1899, **237**, 475—480).—Damascenine is an alkaloid which occurs in the outer coat of the seeds of *Nigella Damascena*, L.; it has been isolated by Schneider (*Inaug. Diss. Erlangen*, 1890), who also prepared some of its salts. The author obtained it by digesting the uncrushed seeds for several days with 6 per cent. hydrochloric acid at 40—50°; the extract was then made alkaline with sodium carbonate and shaken gently with light petroleum, and the alkaloid removed from the petroleum solution (which has a blue fluorescence) by shaking with 8 per cent. hydrochloric acid; the acid extract was concentrated finally at 40°, and the hydrochloride of the alkaloid purified by recrystallisation; the seeds yielded 0·61 per cent. of the pure salt. The platinochloride, $(C_{10}H_{15}O_3N)_2,H_2PtCl_6$, melts and decomposes at 194—198°; the aurichloride is very unstable, decomposing even in the dark. The alkaloid contains two methoxyl groups, and consequently has the formula $C_8H_9ON(OMe)_2$; it resembles methylic anthranilate (Walbaum, this vol., i, 620) closely in many of its properties. C. F. B.

Hydrastine Pentiodide Hydriodide. By HARRY MANN GORDIN and ALBERT B. PRESCOTT (*Arch. Pharm.*, 1899, **237**, 439—446).—See this vol., ii, 826).

Structure of the Alkaloids of the Pomegranate. By ANTONIO PICCININI (*Gazzetta*, 1899, **29**, ii, 104—114. Compare this vol., i, 829).

$$CH_2{-}CH_2{-}CH_2$$
—*Dimethylic methylgranatate,* $COOMe \cdot CH \cdot NMe \cdot CH \cdot CH_2 \cdot COOMe,$

forms an almost colourless oil of a pungent, ethereal odour; it is soluble in dilute acids, gives no precipitate with platinic chloride, but with auric chloride forms a yellowish, oily precipitate. It combines slowly with methylic iodide, yielding *dimethylic methylgranatate methiodide*, $C_{11}H_{19}O_4N,MeI$, which separates from alcohol in colourless prisms melting at 167°; it is soluble in cold water, and its solution in dilute sulphuric acid decolorises permanganate with extreme slowness. On heating this methiodide with alkali hydroxide or carbonate, *dimethylic dimethylgranatenate,*

$$COOMe \cdot CH_2 \cdot CH(NMe_2) \cdot CH_2 \cdot CH_2 \cdot CH{:}CH \cdot COOMe,$$

is obtained as an oil which dissolves in dilute acids, gives an oily *aurichloride* and *picrate*, and combines readily with methylic iodide, forming a *methiodide*, $C_{12}H_{21}O_4N,MeI$, which separates from alcohol in very thin leaflets melting at 143—144°. Dimethylic dimethylgranatenate in dilute sulphuric acid solution instantly decolorises permanganate solution. On boiling the methiodide with concentrated caustic alkali, trimethylamine and *homopiperilenedicarboxylic acid*, $C_2H_4(CH \cdot CH{:}COOH)_2$, are obtained. The latter separates from

water in slender, microscopic, colourless needles melting at 228° with previous softening ; when dissolved in dilute sodium carbonate solution, it is instantly oxidised by permanganate solution. Its *silver salt*, $C_8H_8O_4Ag_2$, forms a white powder which is insoluble in water and suffers change on exposure to light. On reducing homopiperilene-dicarboxylic acid in caustic alkali solution by means of sodium amalgam, normal suberic acid is obtained. T. H. P.

Methylgranatylamines. By ANTONIO PICCININI and A. QUARTAROLI (*Gazzetta*, 1899, **29**, ii, 115—123).—*Methylgranatylamine*, $C_9H_{18}N_2$, obtained by reducing methylgranatonine oxime by means of sodium amalgam and acetic acid, is a dense, colourless liquid which has a faint, basic odour, and at the ordinary pressure boils at 235—240° with slight decomposition, but boils unchanged at 160—170° under 60 mm. pressure. It is very soluble in water, and rapidly absorbs carbonic anhydride from the air with formation of a crystalline mass of carbamate. The *hydrochloride* forms a colourless, deliquescent mass, and the *aurichloride*, $C_9H_{18}N_2,2HAuCl_4$, separates in tufts of yellow needles melting with slight decomposition at 226°, and soluble in boiling dilute hydrochloric acid ; the *platinochloride* is deposited in golden-yellow spangles, which melt and decompose at 260—261°, and are very soluble in dilute hydrochloric acid even in the cold. The *picrate* crystallises from dilute alcohol in thin, golden-yellow leaflets, which melt with decomposition and evolution of gas at 239—240°. By the action of equal parts of the base and of phenylthiocarbimide, *methylgranatylphenylthiocarbamide*, $C_9H_{16}N \cdot NH \cdot CS \cdot NHPh$, is obtained ; it crystallises from ethylic acetate in compact, colourless prisms which melt with previous softening at 132—133°, and are soluble in methylic or ethylic alcohol or in acetone, but insoluble in water.

When methylgranatonine oxime is reduced by sodium and amylic alcohol, *ψ-methylgranatylamine* is obtained as a dense, colourless oil boiling at 232—236° at the ordinary pressure ; it is soluble in water, has an intense alkaline reaction, and absorbs carbonic anhydride, yielding a crystalline *carbamate* melting at about 123°. The *aurichloride*, $C_9H_{18}N_2,2HAuCl_4$, crystallises from dilute hydrochloric acid in yellow needles melting with incipient decomposition at 231—232° ; the *platinochloride* separates from dilute hydrochloric acid in bundles of needles melting and decomposing at 265°. The *picrate* forms a microcrystalline powder which melts with strong decomposition at 239—240°. *ψ-Methylgranatylphenylthiocarbamide*, $C_{16}H_{23}N_3S$, crystallises from ethylic acetate in very slender, colourless needles which melt at 176° and are insoluble in water.

When boiled for a long time with a 30 per cent. caustic soda solution, or with an amylic alcoholic solution of sodium amyloxide, methylgranatylamine is transformed into the ψ-compound.

The relations between these two methylgranatylamines are the same as those existing between the two tropylamines obtained by Willstätter and Müller (Abstr., 1898, i, 492). T. H. P.

β-Morphimethine. By EDUARD VONGERICHTEN (*Ber.*, 1899, **32**, 2379—2380).—The acetate of a tertiary base, *β-morphimethine*, is

obtained on adding ammonia to the filtrate from the non-nitrogenous decomposition products formed when diacetylmorphol is prepared by the action of acetic anhydride on morphinemethylhydroxide (this vol., i, 649). The *hydrochloride*, $C_{18}H_{21}O_3N,HCl + H_2O$, prepared by hydrolysing the acetate with dilute hydrochloric acid, separates in white needles, dissolves readily in cold water and in methylic or ethylic alcohol; concentrated sulphuric acid dissolves it, forming a cherry-red solution which becomes blue when heated or moderately diluted, but intensely green if very largely diluted.

Soda produces no precipitate when added to an aqueous solution of the hydrochloride, but there results a bluish-green fluorescence resembling that of an alkaline solution of morphenol. Ammonia liberates the base in the form of a greenish, flocculent precipitate insoluble in ether, and by adding sodium methoxide in calculated amount to an alcoholic solution of the hydrochloride, the base is obtained as a brown syrup, which ultimately crystallises on treatment with ether. A *methiodide* is readily obtained, which is insoluble in absolute alcohol, but readily soluble in water; the derived ammonium base is not so unstable as the corresponding compound of β-methylmorphimethine.

When morphimethine hydrochloride is heated with an alcoholic solution of sodium methoxide and methylic iodide, the methiodide of β-methylmorphimethine is obtained. A. L.

Alkaloids from Yohimbehe Bark. By LEOPOLD SPIEGEL (*Chem. Zeit.*, 1899, 23, 59—60 and 81—82. Compare *ibid.*, 1896, 20, 970, and 1897, 21, 833; and Thoms, Abstr., 1898, i, 455).—Yohimbehe bark contains a dye and two alkaloids, *yohimbine* and *yohimbinine*. Yohimbine, $C_{23}H_{32}O_4N_2$ or $C_{22}H_{30}O_4N_2$, is a tertiary base and crystallises from dilute alcohol in glistening, white needles, and is readily soluble in alcohol, ether, chloroform, acetone, &c., but only sparingly in water. Its specific rotatory power in alcoholic solution is $[\alpha]_D$ 50·9°. When heated at 120—130°, or when dissolved in absolute alcohol and evaporated to dryness, it appears to be converted into the anhydroform, $C_{23}H_{30}O_3N_2$ or $C_{22}H_{28}O_3N_2$.

The *hydrochloride*, $C_{23}H_{30}O_3N_2,HCl$ or $C_{22}H_{28}O_3N_2,HCl$, is the only salt which has been obtained in a crystalline form; it melts at 295—300°, but at the same time undergoes decomposition.

The *methiodide* is readily soluble in hot water, but only sparingly in cold; it is usually deposited as a syrup which slowly crystallises. An acetyl derivative melting at 133° has been prepared and the action of hydrochloric, hydriodic, and nitric acids on the alkaloid has been studied, but no definite products have been obtained. Oxidation with potassium dichromate and sulphuric acid yields carbonic anhydride and formic acid, whilst potassium permanganate in alkaline solution gives a small quantity of an *acid* melting at 85° and soluble in ether, and two acids insoluble in ether; the one, *yohimbic acid*, $C_{20}H_{24}O_6N_2$, is soluble, and the other, *noryohimbic acid*, $C_{19}H_{20}O_7N_2$, insoluble in cold alcohol. Although the alkaloid probably contains the aldehydo-group, it was found impossible to obtain an oxime or phenylhydrazone.

Yohimbinine has not been obtained as yet in a state of purity; it can be freed from yohimbine by repeated solution in ethylic acetate, from which the latter crystallises, whilst yohimbinine remains in solution. It may be further purified by conversion into its hydriodide, but is still probably not homogeneous, since different specimens have very different melting points. Yohimbine yields a reduction product crystallising in glistening needles and decomposing at 106—108°.   J. J. S.

Pectin from the Fruit of the Wild-Rose. By ÉMILE BOUR-QUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1899, [vi], **10**, 5—10. Compare this vol., i, 652).—The pectin was obtained from the cynorrhodons or fruit of the wild-rose (*Rosa canina*), either by maceration with water and precipitation with alcohol, or by treatment in an autoclave heated to 110°. It forms a light yellow powder which is entirely soluble in water. Its solutions are dextrorotatory, $[a]_D + 165°$, and, like those of other pectins, are coagulated by pectase, lime-water, baryta-water, caustic soda followed by hydrochloric acid, or by neutral or basic lead acetate. A precipitate is formed when its solution is saturated with magnesium or ammonium sulphate, and with ferric chloride the precipitate produced is coloured greenish-black, due to the presence of a tannin-like substance. When pectinase is added to an aqueous solution of the pectin, reducing substances are produced, and the solution is no longer coagulated by pectase. When the coagulum obtained by adding pectase to a solution of the pectin is treated with pectinase, it almost entirely dissolves, and reducing substances are produced.

H. R. LE S.

Action of Heat on Pepsin. By V. HARLAY (*J. Pharm.*, 1899, [vi], **10**, 105—108).—When pepsin, dried at 50°, is heated at 100° for $3\frac{1}{2}$ hours, its digestive action is not changed, but its digestive power is, perhaps, slightly diminished. This confirms the statements of Schmidt (*Centr. med. Wiss.*, 1876, 29) and Salkowski (*Virchow's Archiv.*, 1880, **81**, 552). The activity of an aqueous solution of pepsin is diminished by heating it at 60° for half an hour, and the enzyme is destroyed at about 68°.   H. R. LE S.

Action of Heat on Trypsin. By V. HARLAY (*J. Pharm.*, 1899, [vi], **10**, 166—169).—The digestive power and digestive action of dry pancreatin are in no way diminished or modified by heating it at 100° for $3\frac{1}{4}$ hours (compare Schmidt, *Centr. med. Wiss.*, 1876, 29; Salkowski, *Virchow's Archiv.*, 1877, **70**, 158). Its aqueous solution, however, partly loses its digestive power when heated at 55° for $1\frac{1}{2}$ hours, and the enzyme is destroyed at a temperature of about 60°.

H. R. LE S.

Invertin. By W. A. OSBORNE (*Chem. News*, 1899, **79**, 277—280). —Invertin was prepared from yeast by extraction with 96 per cent. alcohol; the solution was evaporated, and the residue again extracted with chloroform water for six days at 35°. The mixture was ultimately filtered and the filtrate dropped into 96 per cent. alcohol. The precipitated invertin was washed once with absolute alcohol and dried in a vacuum over sulphuric acid; it still contained about 50 per cent. of inorganic admixture, consisting chiefly of potassium and

magnesium phosphates. For details of the methods of purification, the original must be consulted. The final product was an extremely light powder of whitish-grey colour, readily soluble in water and having invertive power of a high order and, by the lowest determination, 1·83 per cent. of ash. Various analyses indicate the average percentage composition of invertin to be C 44·54 ; H 6·52 ; N 6·1. The low percentage of carbon places invertin apart from the proteids ; moreover, it gives negative results with the majority of reagents for detecting proteids ; it, however, reacts faintly with copper sulphate, Millon's reagent, and the biuret test, and more decisively with lead acetate, alcohol, phosphotungstic and phosphomolybdic acids, and the xanthoprotein test.   There is a suggested resemblance to chitin, inasmuch as the analytical numbers are not very different, and after boiling for a few minutes with strong or slightly dilute hydrochloric acid, invertin yields a reducing solution which, when treated with phenylhydrazine, gave a compound having the composition of phenylglucosazone, but melting at 198° instead of 205°.   D. A. L.

Composition of Albumin of the Carob Seed (Ceratonia Siliqua). By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1899, 129, 391—393. Compare this vol., i, 839).—The results of further investigation of the products of hydrolysis of Carob seeds with 3 per cent. sulphuric acid at 110° prove that mannose and galactose are the only sugars formed, the product consisting of 83·5 per cent. of mannose and 16·5 per cent. of galactose.

When hydrolysed as above, 1/8 to 1/7 of the albumin taken is not acted on ; this residue, on treatment with a cold mixture of sulphuric acid and water (3 : 1), after diluting largely and boiling for two hours, yields a sugar which consists almost entirely of mannose, and from which galactose is absent.

The mannose and galactose are present in the albumin as anhydrides of mannose and of galactose (mannans and galactans), the greater part of the former and the whole of the latter being present as hemicellulose.   H. R. LE S.

Sugar from Albumin. By FRIEDRICH MÜLLER and JOHN SEEMANN (*Chem. Centr.*, 1899, i, 1130 ; from *Deutsch. med. Woch.*, 25, 209—211). —The sugar formed from albumin in diabetes does not exist preformed in the albumin molecule, but is produced from the atomic complexes containing nitrogen by a process of oxidation with elimination of nitrogen.   Seemann is stated to have prepared a hexose from albumin identical with Ledderhose's glucosamine before Blumenthal and Mayer did so (this vol., i, 465, 787).   E. W. W.

Sugar from Albumin. By FERDINAND BLUMENTHAL and PAUL MAYER (*Chem. Centr.*, 1899, i, 1131 ; from *Deutsch. med. Woch.*, 25, 211. Compare preceding abstract).—A reply to Müller and Seemann's claim for priority.   E. W. W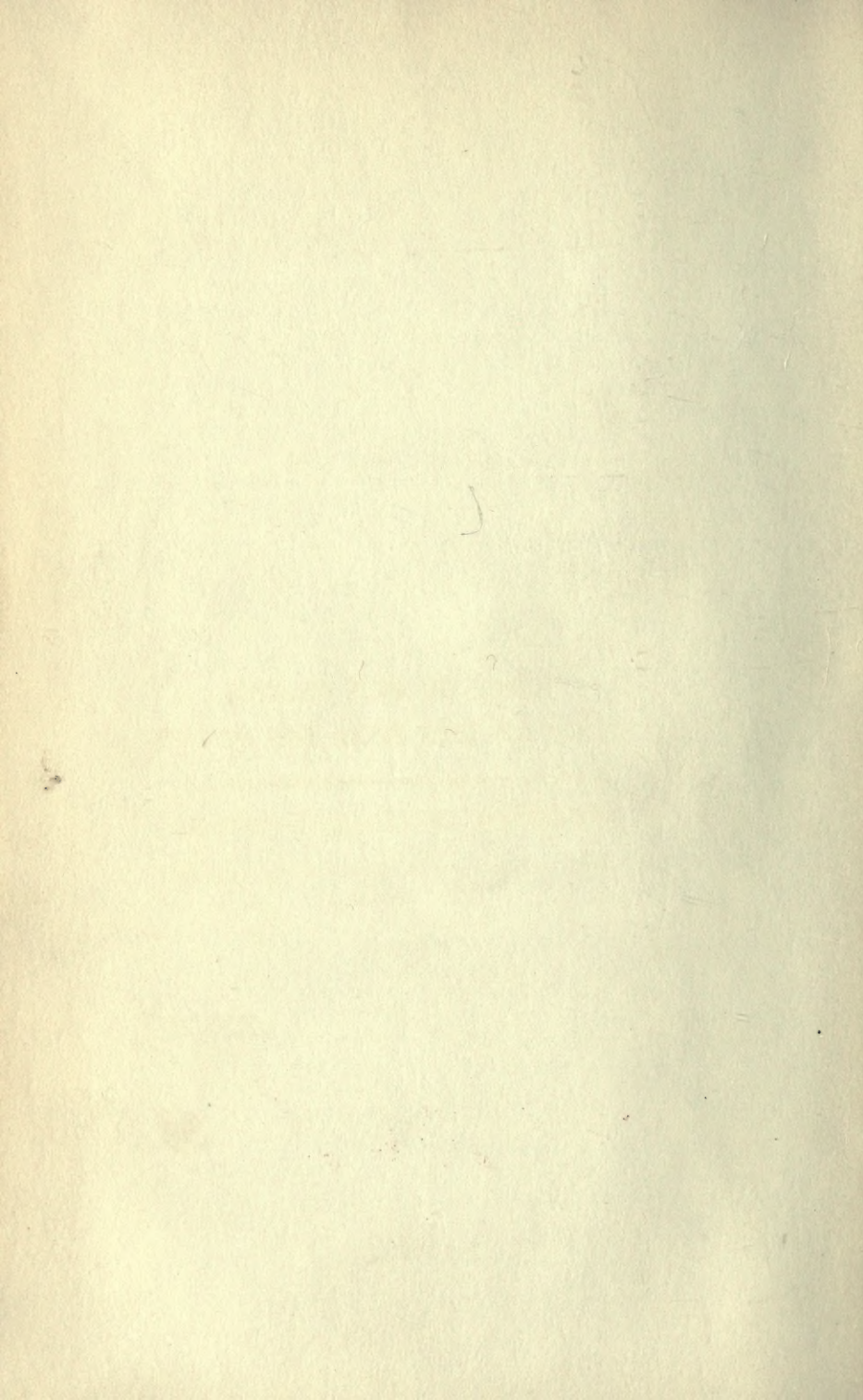.